Chain Processes in the Tc(VII)-Catalysed Oxidation of Hydrazine by Nitrate and Perchlorate Ions

by

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Dedicated to my wife Alison, my family and friends

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ABBREVIATIONS

1AR	column 1A raffinate or waste solution
1AS	column 1A solvent scrubbing state.
1AX	column 1A solvent extraction stage
BNFL	British Nuclear Fuels plc.
1 B.P.	solvent product from column 1B containing purified Pu
1B.X.X.	column 1B second solvent extraction stage.
Column 1A	the first bank of three solvent extraction columns.
Column 1B	the second bank of three solvent extraction columns.
Column 1C	the third bank of three solvent extraction columns.
1.C.R.	spent solvent from column 1C
1CU	an aqueous nitric acid stream from column 1C containing purified uranium.
e.s.r.	electron spin resonance spectroscopy
F.P's	fission products
g.c.m.s.	gas chromatography mass spectroscopy
G	Gauss
H.A.	high active, highly radioactive
HAN	hydroxyamine nitrate
Magnox fuel	a fuel made of non-enriched uranium metal which contains less than 1% ^{235}U for use in Magnox reactors.
mins	minutes
ms	millisecond
Nox	nitrogen oxides
O.K.	odourless kerosine
org	organic
ox	oxidised

oxide fuel	a fuel for use in gas cooled reactors or light water reactors which consists of uranium oxide pellets which have been enriched to increase the ^{235}U content to 2-3%
PBN	benzylidine nitrone
PDMAB	para-dimethylaminobenzaldehyde
P.R.	plutonium purification
PUREX Process	Plutonium Uranium Recovery by Solvent Extraction.
Raffinate	term for discribing a waste solution in nuclear fuel reprocessing
s	seconds
THORP	Thermal Oxide Reprocessing Plant
THORP Process	modified PUREX process to be utilised in the THORP plant
TBP	Tri-n-butylphosphate
UP	uranium purification
U.V.-vis.	ultra violet and visible spectroscopy
λ_{max}	absorption maximum of U.V. or visible light by a molecule or ion
μ	ionic strength of a solution

ABSTRACT

Studies of the reaction between pertechnetate ion and hydrazine in solutions in several different acids have been carried out in order to establish the reaction mechanism and, where possible, the individual rate constants of each step. Computer simulation of the experimental data has been utilised to enable the formulation of reaction schemes for these very complex chain reactions.

In nitric acid the reaction typically exhibits an induction period of variable length depending on the acidity and concentrations of nitrate, hydrazine and technetium. This is followed by a stage of rapid loss of hydrazine from the solution due to its oxidation by Tc^{VI}, while the Tc^{IV} produced is re-oxidised to Tc^{VI} by nitrate. The termination step is considered to be the acid-catalysed oxidation of Tc^{VI} to TcO_4^- by nitrate. The effect of increasing acidity is to increase the length of the induction stage and to decrease the rate of hydrazine oxidation during the fast reaction stage; this causes the reaction to be terminated with increasingly greater residual concentrations of unoxidized hydrazine; at 5 mol dm^{-3} HNO_3 no loss of N_2H_4 from the solution is observed.

Replacing nitric acid by acids such as $HClO_4$, HBF_4, HCl or CF_3COOH shows that nitric acid is unique in its inhibiting effect on the hydrazine destruction reaction. In the presence of these acids the length of the induction stage is decreased, and the rate of the fast reaction stage is increased, with increasing acidity, i.e. in direct contrast to the situation for HNO_3 media

A reaction scheme has been proposed for the complex of processes that occur in perchloric acid or tetrafluoroboric acid-sodium nitrate media. In these systems it is proposed that the increases in the reaction rates with increasing acidity is due to protonation of the highly reactive Tc^{VI} species, which is stabised towards oxidation to TcO_4^-, i.e. the essence of the termination process.

The kinetic situation in perchloric acid appears to be even more complex, and several intermediate complexes of Tc^{IV} appear to be produced. It is proposed that the sharp peak in the time-profile of the concentration of Tc^{IV} at the onset of the fast reaction stage is due to the presence of the $TcO(OH)_2$ complex. In later stages of the reaction the hydroxide ligands are replaced by chloride ion, which is produced by the reduction of perchlorate. The oxochlorotechnetium(IV) complexes so produced are more resistant to oxidation than simple oxo complexes and are not re-oxidised to TcO_4^- on termination of the reaction. The computer simulation of these results has led us to invoke the production of an intermediate Tc^{III} complex.

The results of the work in HNO_3 and $HClO_4$ media were presented as an oral communication at the Third International Symposium on Technetium in Chemistry and Nuclear Medicine held at Montegrotto Terme in September 1989. The abstract included in the conference proceedings is presented in the appendix.

CONTENTS

1.1 Isotopes of Technetium

Technetium, element 43, was the first element to be produced artificially before it was discovered in nature. It was discovered in 1937 by Carlo Perrier and Emilio Gino Segre in a molybdenum target that had undergone bombardment by deuterons in the Berkeley cyclotron.

Thirty one isotopes of technetium have been discovered, all of which are radioactive with half lives ranging from 0.82 seconds to 4.2 x 10^6 years. The half-life of the longest-lived isotope is still too short for the element to have persisted in the earth's crust since genesis. Only traces of naturally occurring technetium have been found. In 1961 Kenna and Kuroda (1) reported finding 1 ng of ^{99}Tc in 5.3 kg of Belgian Congo pitchblende, formed by the decay of daughter elements produced in the spontaneous fission of ^{238}U.

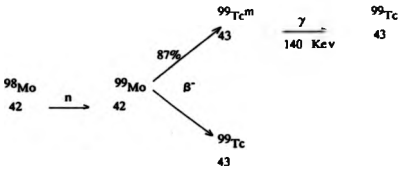
The only isotope of interest is ^{99}Tc, together with the widely-utilised ^{99m}Tc, the latter being produced in hundreds of millions of curies per year for medicinal use. In the field of diagnostics and organ imaging, it is the most important and widely used radiopharmaceutical. Nearly all ^{99m}Tc for medical use is obtained as a decay product of ^{99}Mo; the latter is obtained from the fission products of ^{235}U.

^{99}Tc with a half-life of 2.14 x 10^5 years is the only isotope obtained in kg amounts. It is produced in 6.1% yield as a decay product of a fission product of ^{235}U according to the sequences overleaf.

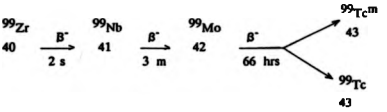
1.2 The Redox Chemistry of Technetium

Technetium, a member of the manganese triad, is generally considered to have the outer electronic ground state configuration $(Kr)4d^65s^1$ (4); Rossotti et al. however, proposed a configuration of $(Kr)4d^55s^2$

Decay sequences leading to the production of ^{99}Tc and $^{99}Tc^{m}$.



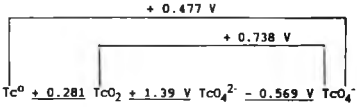
From Ref. (2)



From Ref. (3)

(5). A variety of oxidation states is possible from 7 to -1. The nature of technetium species in aqueous solutions is governed not only by a set of oxidation reduction reactions, but also by disproportionation, hydrolytic and complexation equilibria, polymerisation and colloid formation.

Pertechnetate $[TcO_4]^-$ is the most important and stable oxidation state of technetium, especially in aqueous solution, being stable over a wide pH range (unlike permanganate but like perrhenate). Pertechnetate is correspondingly a much weaker oxidant than permanganate; the standard electrode potential for MnO_4^-/MnO_2 is +1.695 V (6) and that for TcO_4^-/TcO_2 is + 0.738 V. The redox potentials for some oxidation states of technetium are shown diagramatically below; these values refer to an acidic solution at 298 K (7).



Hydrazine is a moderately strong reducing agent, the standard oxidation-reduction potential of the $N_2H_5^+/N_2$ pair in an acidic environment being given as -0.23 V (8). However, the potential given recently by Koltunov et al. for a 1.0 M nitric acid environment is +0.3 V (9); it can be expected therefore that in nitric acid media hydrazine would be capable of reducing TcO_4^- to TcO_2.

Disproportionation Reactions

Some of the oxidation states of technetium are highly reactive and display tendencies towards disproportionation, this tendency being

greatly affected by pH and the presence of complexing agents. Some of the disproportionation reactions proposed for technetium are given in Table 1.1.

Technetium^{VI}, in the form TcO_4^{2-} (technetate ion) is unstable with respect to Tc^{IV} and Tc^{VII} in alkaline, neutral or acidic media (7,10-12,25). The obviously probable products of the disproportionation of Tc^{VI}, equation 1.1, are Tc^{VII} and Tc^{V}. This disproportionation reaction is thought to play an important role in the electrochemical reduction of TcO_4^- (17). The technetate ion is also unstable with respect to disproportionation in organic solvents containing traces of water (14).

Tc^{V} in an uncomplexed form is also unstable both in aqueous solution and damp organic solvents, disproportionating to Tc^{IV} and Tc^{VII} according to equation 1.2. Many Tc^{V} complexes with polydentate ligands are stable with respect to disproportionation and can be isolated.

In 1964 Ossicini et al. (18), showed that Tc^{V} is produced when TcO_4^- and $TcCl_6^{2-}$ are allowed to stand in dilute HCl for 2-3 days. This supports the view of Garraway and Wilson (15) that Tc^{VII} and Tc^{IV} react to give Tc^{VI} and Tc^{V} (equation 1.3).

The uncomplexed form of Tc^{V} is also thought to disproportionate according to equation 1.4 giving Tc^{VI} and Tc^{IV}.

Technetium(VII)

In aqueous solutions the commonest species is the tetrahedral pertechnetate ion, TcO_4^-. Pertechnetic acid is a strong acid in aqueous solution, the published values of its pKa varying from -8 to +0.2 (19-23). The red colouration produced on dissolving Tc_2O_7 or $HTcO_4$ in aqueous solutions has been attributed to the presence of the undissociated acid.

TABLE 1.1

Disproportionation Reactions of Technetium

EQUATION	RATE OF REACTION	AUTHOR
[1.1] $3\ TcO_4^{2-} + H_2O \longrightarrow 2\ TcO_4^- + TcO_3^{2-} + 2OH^-$	1.5×10^5 dm^3 mol^{-1} s^{-1} (10)	12, 13, 16
	3×10^6 dm^3 mol^{-1} s^{-1} (13)	10
[1.2] $3\ TcO_3^- + H_2O \longrightarrow TcO_4^- + 2TcO_3^{2-} + 2H^+$		14
[1.3] $Tc^{IV} + TcO_4^- \longrightarrow Tc^V + Tc^{VI}$	2.78 mol dm^{-3} s^{-1}	15
[1.4] $2\ Tc^V \longrightarrow Tc^{VI} + Tc^{IV}$		16

Literature U.V.-vis. spectra of the species $HTcO_4$-TcO_4^- and Tc_2O_7 are given in figures 1.1 (19) and 1.2 (24). The spectrum of $HTcO_4$ (figure 1.2) displays a peak at 208 nm in addition to the two peaks due to the pertechnetate ion at 244 and 287 nm.

In 7-11 M perchloric or sulphuric acids the species Tc_2O_7 is produced, figure 1.1, the peak at 287 nm due to TcO_4^- being replaced by a broad peak centred around 340 nm attributed to the heptoxide.

The production of the species TcO_3^+ in the technetium-hydrazine reaction has been postulated by Koltunov et al. (25) by analogy with the production of the manganate ion, MnO_3^+, in sulphuric acid solution (26). Garraway and Wilson (27) also postulated the acid-dependent production of a Tc^{VII} species from the TcO_4^- ion.

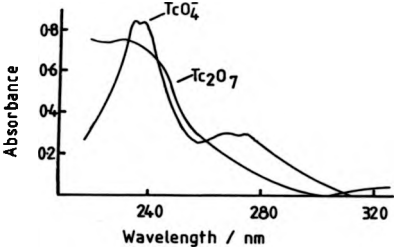
Technetium(VI)

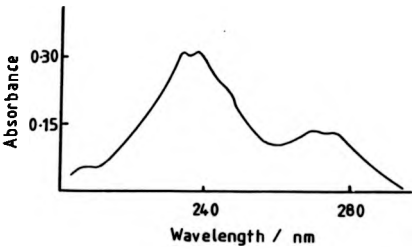
Several halides and oxohalides of Tc^{VI} exist including TcF_6 (28) and $TcOF_4$ (29). The oxide TcO_3 has been prepared (11.30.31) and reacts readily with water giving $HTcO_4$ and TcO_2 (11).

The production of the technetate ion, TcO_4^{2-} has been reported during the reduction of pertechnetate at a mercury electrode (10). Libson et al. generated Tc^{VI} electrochemically and found it to be stable for 10 ms in 0.12 M NaOH (32); it is also possible to stabilise it by adding gelatin (10). The pulse radiolysis of pertechnetate ion in aqueous alkali produces the technetate ion (33). It was shown that the decay of this transient was highly dependent on pH; thus at pH 10 there was no detectable decay during the period of their experiment (several milliseconds), in neutral media it decayed at a measurable rate and in acidic solution (pH < 4) the reduction of pertechnetate by $H^\cdot$ rapidly yielded polymeric TcO_2. The U.V-vis. spectrum of this Tc^{VI} species shows a broad absorbance centred around 500 nm and a peak at 340 nm (34). Several salts of Tc^{VI} have

Figure 1.1 : U.V.-Visible Spectrum of TcO_4^- and Tc_2O_7

Figure 1.2 : U.V.-Visible Spectrum of $HTcO_4$


TcO4-
Tc2O7
0·8
0·6
0·4
0·2
Absorbance
240
280
320
Wavelength / nm


0·30
0·15
Absorbance
240
280
Wavelength / nm

been isolated as solids, some of these being $BaTcO_4$ (35), $[(CH_3)_4N]_2TcO_4$ and K_2TcO_4 (36). Violet compounds of TcO_4^{2-} in non-aqueous solution decompose in the presence of oxygen and moisture (37).

A Russian group has investigated the kinetics of the oxidation of Pu^{III} in nitric acid solution by Tc^{VI} in the presence of hydrazine (38) and hydrogen peroxide (39). No indication as to the nature of the Tc^{VI} species produced is given in either of the papers. They do, however, give several U.V-vis. spectra, and one of the purported spectra of Tc^{VI} is given in figure 1.3. This shows a peak at 231 nm, but no details of the spectrum in the visible region of the spectrum are given. Clearly the Tc^{VI} species produced cannot be the technetate ion, if indeed the product is Tc^{VI}. No consideration is given of the widely-known tendency for Tc^{VI} to disproportionate in aqueous solution in either of these studies.

Tc^{VI} does, however, form some stable complex ions capable of existing in aqueous systems. The nitride ligand (N^{3-}) is a powerful π-electron donor which tends to stabilise metals in high oxidation states. Several of its complexes with Tc^{VI} have been characterised, for instance $[TcNCl_4]^-$ (39) and $[TcNBr_{4-p}\ Cl_p]^-$ (p = 1-3) (40).

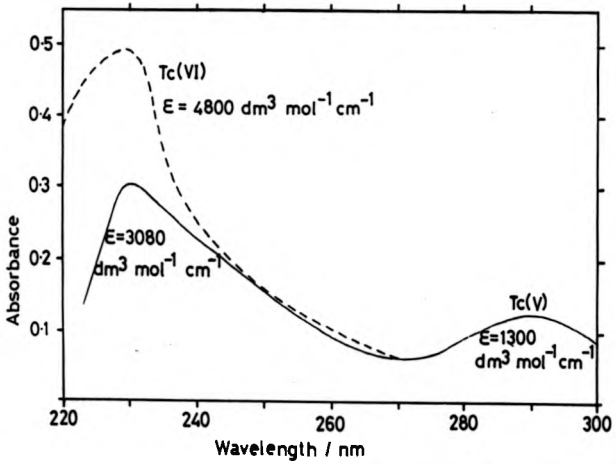
Technetium(V)

This has a quite well-developed chemistry with a range of halides and oxohalides being established, for example TcF_5 and TcF_6^- and $TcOCl_3$ (41.42). The addition of pertechnetate ions to concentrated hydrochloric or hydrobromic acids reduces TcO_4^- to the $[TcOX_y]^{x-}$ ion where X = Cl, Br; y = 4-5; x = 1 or 2). This reduction is thought to occur via the intermediate Tc^{VII} state $[TcO_3Cl_3]^{2-}$. Attempts to isolate this salt have however failed. Substitution products with non-reducing ligands have, on the other hand, been isolated, for

Figure 1.3 : U.V.-Visible Spectrum of Tc^{VI} and Tc^{V}.
(from ref. 39)

$[HClO_4]$: 3.0 mol dm^{-3}

[Tc) : 1 x 10^{-4} mol dm^{-3}


0·5
0·4
0·3
0·2
0·1
Absorbance
Tc(VI)
E = 4800 dm3 mol-1 cm-1
E=3080
dm3 mol-1 cm-1
Tc(V)
E=1300
dm3 mol-1 cm-1
220
240
260
280
300
Wavelength / nm

instance, $TcO_3Cl(2,2\text{-bipyridine})$ (43).

The oxotechnetate(V) complexes can be categorized on the basis of their oxotechnetium cores, (44) thus : (a) TcO^{3+}, (b) trans-TcO_2^+ and (c) $Tc_2O_3^{4+}$. The fourth type $Tc_2O_2^{6+}$ is simply a polymeric form of (a).

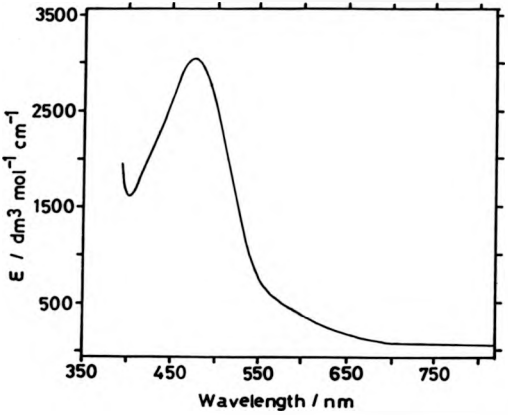
Spitsyn et al. (16) have isolated and identified a solid product $TcO(NO)_3)_3$ produced in the explosive reaction between high concentrations of hydrazine and TcO_4^- in concentrated nitric acid. In concentrated $HClO_4$ solutions the complex had a cationic form (λ_{max} 500 nm), in concentrated HNO_3 solution a neutral form (λ_{max} 470 nm) and in 0.5 M HNO_3 a mixture of cationic, neutral and anionic forms. This production of a Tc^V species with the TcO^{3+} featuring λ_{max} 470 nm correlates well with the species thought to be TcO^{3+} produced by Zelverte (2) with λ_{max} 474 nm, produced in the electrochemical reduction of pertechnetate. The U.V.-vis. spectrum of Zelverte's complex is given in figure 1.4. Another spectrum of a Tc^V species is given in figure 1.3; this species was produced by Borovinskii et al. (39) by reduction of Tc^{VI} with Pu^{III}.

Technetium(IV)

Technetium (IV) is the second most important oxidation state of technetium, forming a wide range of binary compounds such as TcO_2, TcS_2 and halides, for example $TcCl_4$ (45). A large number of complexes of technetium(IV) have been observed, for example, the analytically well-known thiocyanate complex $[Tc(SCN)_6]^{2-}$ which is formed in aqueous solution by the reaction between Tc^V and ammonium thiocyanate.

The nature of the technetium ion in aqueous solution depends on prevailing conditions. Rard (37, p.42) has suggested the existence of the Tc^{4+} aquo ion in very strongly acidic solution. In an acidic

Figure 1.4 : U.V.-Visible Spectrum of the TcO^{3+} ion.


3500
2500
1500
500
ε / dm3 mol-1 cm-1
350
450
550
650
750
Wavelength / nm

perchlorate medium Tc^{IV} has a charge of +2 and presumably exists as TcO^{2+}.

Tc^{IV} compounds are however prone to hydrolysis giving species such as $TcO(OH)_2$, $[TcO(OH)]^+$ and $[Tc(OH)_2]^{2+}$ (46, 47).

The oxide $TcO_2.2H_2O$ is sparingly soluble in water-based media and the nature of the species produced on its dissolution is uncertain, although several ideas have been proposed. Spitsyn (48) dissolved the oxide in 0.71 M H_2SO_4 and obtained a brown complex given as $[Tc(OH)_2(SO_4)_2]^{2-}$. Rard designated this species as $[TcO(SO_4)_2]^{2-}$, whilst Noll et al. (37, p.41) found that Tc^{IV} exists predominantly as a colloid above pH 0.5.

Technetium(III)

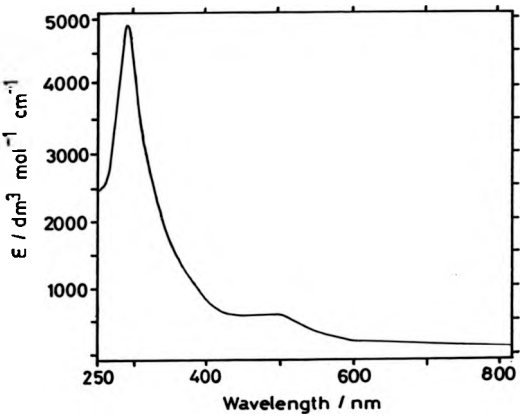
There are many reports of the strongly reducing technetium(III) in aqueous solution. Tc^{III} is reported to disporportionate to Tc^{IV} and Tc^0 above pH 4 (37, p.49; 49, 50). It is possible, however, to stabilise it with complexing agents such as tripolyphosphate (51), phosphate (49) and carbonate (52) ions.

Technetium(III) can be readily oxidised to Tc^{IV} (53, p.897). Zelvarte (2) carried out a spectrophotometric study to determine the rate of oxidation of the Tc^{III} species TcO^+ by nitrate ion with varying temperature, acidity and nitrate ion concentration and obtained an activation energy of 46.5 kJ mol^{-1} for the reaction. The U.V-vis spectrum of the species he assigned as either TcO^+ or $Tc(OH)_2^+$ is given in figure 1.5. This red-orange species displays an intense peak at 290 nm and a shoulder at 500 nm.

Many complexes of Tc^{III} are stable, while Munze (54, p.163) and Terry and Zittle (55, p.66) note that certain complexes are easily oxidised by air to Tc^{VII}.

Some Tc^{III} species act as useful precursors, for example, the

Figure 1.5 : U.V.-Visible Spectrum of the TcO^{+} ion. Prepared by the Electrochemical Reduction of Tc^{IV} at a Mercury Electrode and a Potential of -0.25 V vs. SCE (from ref. 2)


5000
4000
3000
2000
1000
ε / dm³ mol⁻¹ cm⁻¹
250
400
600
800
Wavelength / nm

thiourea complex $[Tc(thiourea)_6]Cl_3$ has been used for the synthesis of $[TcCl_2(diphos)_4]$ and $[Tc(NCS)_6]^{3-}$ (56). It has also been used to synthesise a variety of hexakisalkylisonitriletechnetium(I) cations, $[(RNC)_6Tc(I)]^+$ by treatment with an excess of the isonitrile (57).

Technetium(II)

Technetium(II) does not seem to exist as a hydrated Tc^{2+} aquo ion except in the absence of complexing agents and in highly reducing acidic solutions (57, p.2). Thus Armstrong and Taube reported the production of a pink transient with a lifetime of several seconds in the reduction of pertechnetate with the Eu^{2+} ion in very acidic media, (37, p.48, 54) which they asssumed was Tc^{2+}.

Otherwise Tc^{II} seems to exist only as very stable complexes. The first divalent technetium species to be isolated were the complexes $Tc(diars)_2X_2$. [diars = 1,2-bisdimethylarsinobenzene and X = Cl, Br (58)]. Probably the most widely-studied group of Tc^{II} complexes are the nitrosyls, the first being prepared by Eakins et al. (59) (Eakin's pink compound) by reducing $TcCl_6^{2-}$ with hydroxylamine in hydrochloric acid. They incorrectly formulated the pink species as $[Tc(NH_2OH)_2(NH_2)_3]^{2+}$, which was later recognised as $[Tc(NH_3)_4(NO)(H_2O)]^{2+}$ by Armstrong and Taube (60).

The Tc-NO moiety is remarkably stable and a wide variety of compounds have been prepared by ligand exchange reactions starting from $[Tc(NO)Cl_4]^-$.

Technetium (+1,0,-1)

The oxidation states below two are unimportant in aqueous solution. Compounds containing the metal in the plus I oxidation state can be stabilised by good π-bonding ligands such as NO, CO, CN and aromatic hydrocarbons (3, p.316). A range of carbonyls have been produced either containing CO as the sole ligand as in $Tc(CO)_6^+$ or in mixed

ligand complexes, such as $[Tc(CO)_3(pyridine)_2Cl]$.

Most Tc(0) complexes appear to be carbonyls such as $Tc_2(CO)_{10}$ (61, 62) but the complex $Tc(diphos)_2(N_2)$ has also been isolated (63).

It is believed that the previously reported Tc^+ species (64; 65, p.374) produced in the polarographic reduction of pertechnetate are in fact hydride complexes of positive oxidation states (66).

Polynuclear Technetium Complexes

Technetium compounds often display tendencies towards polymerisation, several compounds existing that contain two or more technetium atoms. These range from neutral species such as Tc_2O_7 and Tc_2S_7 to ions such as $Tc_2X_8^{y-}$ where X = Cl, Br and y = -2 or -3 (67, 68). The ion $Tc_3Cl_9^+$ has been observed to form in a mass spectrometer (69) and the complexes $Tc_8I_{13}.2H_2O$ and $Tc_8Br_{13}.2H_2O$ have been studied by X-ray photoelectron spectroscopy by Kryutshkov et al. (70).

Complexes containing infinite chains of technetium atoms have also been characterised. The complex $Tc_2(OC_5H_4N)_4Cl$ forms an infinite chain with each pair of Tc atoms being linked to its neighbour by a bridging Cl^- ion (71).

1.3 The Reprocessing of Irradiated Nuclear Fuel

1.3.1 Separation methods

The separation methods used for the recovery of uranium and plutonium from irradiated fuel are based on the following chemistry.

a) Stabilities of the oxidation states

$$UO_2^{2+} > NpO_2^{2+} > PuO_2^{2+} > AmO_2^{2+} > Pu^{3+} >> Np^{3+},\ U^{4+}.$$

By choice of a suitable oxidising or reducing agent the appropriate oxidation state for precipitation or solvent extraction can be found, as illustrated in the equation below.

$$Pu^{III} + Am^{III} \xrightarrow{NO_2^-} \underset{\text{Remove by solvent extraction}}{Pu^{IV}} + \underset{\text{Precipitate as the fluoride}}{Am^{III}}$$

b) Extractability into organic solvents

Various actinide nitrates are soluble in several organic solvents, such as ethers, but in present commercial operations tri-n-butylphosphate (TBP) is universally used at least for the main separation. It is usually diluted with a hydrocarbon solvent such as dodecane or kerosene to reduce viscosity and density while adjusting the extractive power to a convenient level.

c) Precipitation reactions

M^{3+} or M^{4+} ions can be removed from solution as insoluble fluorides or phosphates.

1.3.2. The recovery of uranium and plutonium

After removal from the reactor, the irradiated fuel rods are placed in a cooling pond for 4-6 months (5 years for oxide fuel), to allow some of the short-lived fission products to decay to an acceptable level, before transport to the reprocessing site, where there is a further cooling period to simplify handling problems due to the extreme radioactivity of the solutions. Such problems increase with

the level of "burn-up" of the fuel.

The fission products that can be separated chemically from the spent fuel consist of over 30 elements. The original isotopes are unstable and undergo a series of 1 to 6 β-decays before a stable isotope is formed. There are generally several per element and the average decay series consist of 3-4 members so several hundred isotopes will be present in a given sample of mixed fission products.

1.3.3 The PUREX process

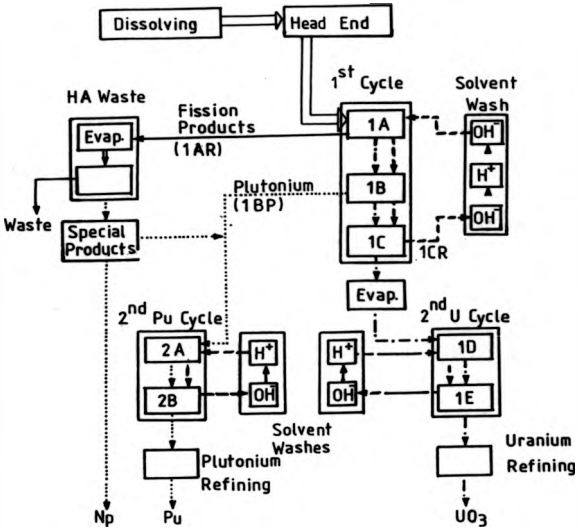
The most widely used method of reprocessing nuclear fuel is the PUREX process.

The name PUREX was derived from Plutonium, Uranium, Recovery by EXtraction. This process can be defined as a counter-current solvent extraction process by tri-n-butylphosphate (TBP) in a nonpolar diluent to separate uranium and plutonium from dissolved nuclear fuels or targets.

The choice of TBP as an extractant has proved to be an excellent one. It has good radiolytic and chemical stability, low solubility in water and its chelating properties make it possible to separate uranium and plutonium not only from fission products and actinide by-products but also from each other to a 99.97% purity level.

Figure 1.6 is a simplified scheme of the PUREX flowsheet in operation at the Savannah River Plant (72). In the first bank of columns (column 1A) the plutonium and uranium are extracted into the solvent as $Pu(NO_3)_4.2TBP$ and $UO_2(NO_3)_2.2TBP$. Most of the fission products and unwanted actinides are rejected to the aqueous waste or raffinate stream, (1AR). The solvent eluant from the first bank contains the desired products and becomes the feed for the second bank.

Figure 1.6 : A Simplified Flowsheet for the PUREX Process


Dissolving
Head End
1st Cycle
Solvent Wash
HA Waste
Fission Products (1AR)
Evap.
1A
OH⁻
H⁺
OH⁻
Plutonium (1BP)
1B
Waste
Special Products
1C
1CR
Evap.
2nd Pu Cycle
2nd U Cycle
2A
H⁺
H⁺
1D
2B
OH⁻
OH⁻
1E
Solvent Washes
Uranium Refining
Plutonium Refining
Np
Pu
UO3

In the second bank (1B), the separation of uranium and plutonium is carried out by reducing plutonium to the almost inextractable Pu^{III}, thus stripping it from the solvent into the aqueous stream (1BP). In bank 1C, the uranium is stripped from the solvent into a low acid stream (1CU)..

The four streams from the first cycle are thus the uranium and plutonium products, each to be further purified; the spent solvent to be washed and recycled; and the aqueous raffinate, 1AR, containing the overwhelming bulk of fission products, which must be stored indefinitely.

Several reductants have been employed in the PUREX process at the reductive separation stage where plutonium is eliminated from the solvent stream by reducing it to Pu^{III}. The reductant initially used for this purpose was iron(II) sulphamate which has the advantage that the Fe^{II} ion very rapidly reduces Pu^{IV} to Pu^{III} even in moderately strong nitric acid. However, there are several disadvantages, thus it is consumed greatly in excess of its stoichiometric requirement, it produces a large volume of effluent that cannot be greatly concentrated without undesirable separation of solids, the sulphate ions produced in its breakdown produce sulphuric acid which causes corrosion problems, it is difficult to accomodate in the vitrified form intended for the more active process wastes and, moreover, plutonium losses are caused by the production of sulphate complexes (73, 84).

Two of the main alternatives to iron(II) sulphamate that have been considered are (1) hydroxylamine nitrate (HAN) and (2) uranous ion (U^{4+}) with hydrazine.

The utilisation of hydroxylamine both as its sulphate and nitrate salts has been investigated by several groups (75 - 78). The use of

the sulphate has been ruled out as its reduction is slow and incomplete apart from the problems associated with sulphate outlined above. HAN has been used successfully in conjunction with iron(II) sulphamate for several years in the Savannah River Plants PUREX facility (75), reducing the required quantities of sulphamate by about 70%. It has also been used as primary reductant, but suffers from an extreme sensitivity to acid.

The U^{IV}–hydrazine combination has been widely investigated (79–81) and is the chosen combination of reductants for use in the Thermal Oxide Reprocessing Plant (THORP) currently being built at Sellafield, U.K.

1.3.4 The process in use in the thermal oxide reprocessing plant

The reprocessing of fuel in THORP is based on a modified PUREX process, thus it relies on the same chemistry and solvent extraction properties of the actinides and fission products already described. Quantitatively, however, the composition of spent oxide fuel is very different from the Magnox fuel reprocessed in the earlier plant owing to differences in manufacture and irradiation. Oxide fuel is irradiated to much higher levels (by factors of roughly 3–10) than Magnox fuel and hence a much higher proportion of fission products and plutonium builds up. This has the consequences that:-

(a) the fuel is much more highly radioactive on emerging from the reactor and requires either a longer cooling period for decay or a design of plant that ensures a briefer contact between the fission products and the solvent to minimise degradation (in fact both are adopted in THORP).

(b) The higher plutonium content (1% against about 0.3%) requires closer control to prevent any possibility of accidental criticality.

(c) The plutonium level also requires a different chemistry of reduction as consumption of ferrous sulphamate would be excessive even if it were capable of the required performance.

A flowsheet for THORP is provided (82) (figure 1.7); the main innovation is the replacement of iron(II) sulphamate with the uranium(IV) - hydrazine combination.

The uranous ion rapidly reduces Pu^{IV} to inextractable Pu^{III}, in the 1B column, according to the following equation;

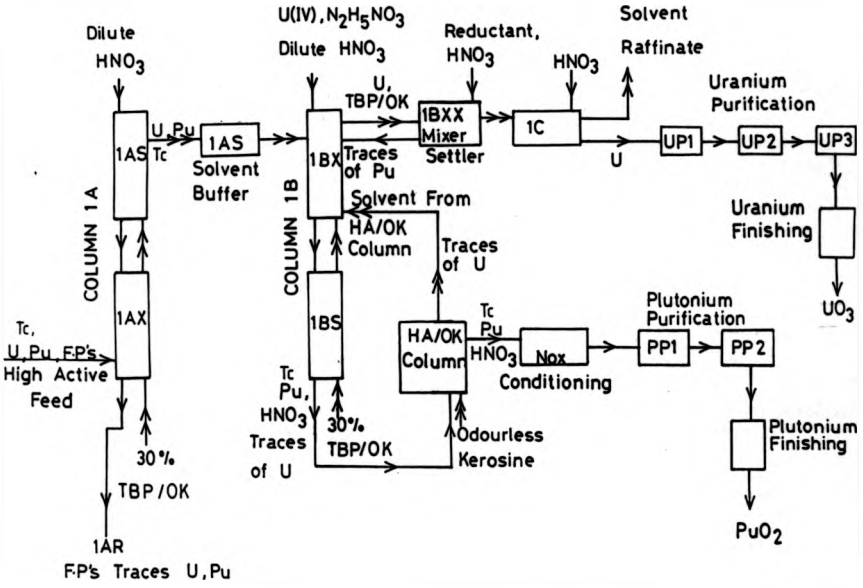
$$2[Pu^{IV}(NO_3)_4.2TBP]_{org} + U^{IV}(aq) \rightarrow$$
$$[U^{VI}(NO_3)_2.2TBP] + 2Pu^{III}(aq) + 4NO_3^- + 2TBP$$

Thus the spent reductant is extracted as U^{VI}, thereby leaving no unwanted residue such as Fe^{III}.

Hydrazine is added to solutions as a stabilising agent, that is, it destroys any nitrite formed (from nitrate) thus preventing the undesirable oxidation of Pu^{IV} to Pu^{III} by the NO_2^- ion. Nitrite is produced in three main reactions, (a) the radiolytic or thermal breakdown of nitric acid, (b) the autocatalytic oxidation of Pu^{III} or U^{IV} and (c) the technetium-hydrazine reaction. The presence of nitrite is highly objectionable as it could lead to incomplete reduction of the Pu^{IV} due either to partial destruction of the U^{IV} reductant or to reoxidation of the Pu^{III} to Pu^{IV}. Both pathways lead to the incomplete removal of Pu from the solvent stream, and hence contamination of the uranium product.

Technetium as ^{99}Tc is a major contaminant in the THORP process due to its coextraction into the solvent stream with uranium or zirconium (see section 1.4). Technetium can catalyse the destruction of hydrazine and uranium(IV) to a considerable

Figure 1.7 : A Simplified Flowsheet of the Modified PUREX Process to be used in THORP.


Dilute
HNO_3
U(IV), $N_2H_5NO_3$
Dilute HNO_3
Reductant,
HNO_3
Solvent
Raffinate
HNO_3
Uranium
Purification
U,
TBP/OK
1BXX
Mixer
Settler
1C
UP1
UP2
UP3
U
1AS
U,Pu
Tc
1AS
Solvent
Buffer
1BX
Traces
of Pu
COLUMN 1A
COLUMN 1B
Solvent From
HA/OK
Column
Traces
of U
Uranium
Finishing
UO_3
1AX
1BS
Tc,
U, Pu, F.P's
High Active
Feed
HA/OK
Column
Tc
Pu
HNO_3
Nox
Conditioning
Plutonium
Purification
PP1
PP2
Tc
Pu,
HNO_3
Traces
of U
30%
TBP/OK
Odourless
Kerosine
Plutonium
Finishing
30%
TBP/OK
1AR
F.P's Traces U, Pu
PuO_2

extent under the conditions found in the 1B column and will thus interfere with the reduction of Pu^{IV} and Pu^{VI}. This topic will be dealt with in detail later (section 1.6)

1.4 The Coextraction of TcO_4^- with U and Zr

The coextraction of pertechnetate by U^{VI} was first reported by Siddal (83) who suggested the following complexation to account for the observation (equation 1.5).

$$UO_2^{2+} + TcO_4^- + NO_3^- + 2TBP \rightarrow [UO_2(NO_3)(TcO_4).2TBP] \quad (1.5)$$

Macasek (84) found that a similar reaction occurs when pertechnetate is extracted from NH_4NO_3 (4 M) by TBP (1 M) in CCl_4. Liester et al. (85) studied the extraction of pertechnetate from a nitric acid-uranyl nitrate aqueous phase and concluded that the extraction of technetium was essentially independent of temperature between 20 and 60°C.

Numerous studies have been carried out to investigate the synergic extraction of mixed nitrate-pertechnetate species in the presence of different metals. Those which have been found to most enhance this coextraction are uranium, zirconium and thorium.

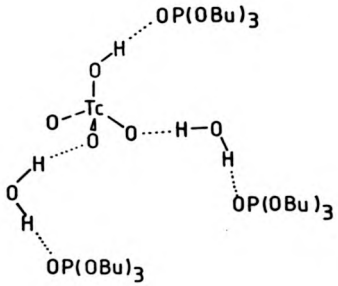
The intrinsic extractability of the pertechnetate ion into tri-n-butyl phosphate-odourless kerosene (TBP-OK) has been shown to be low (86); these results show that most of the Tc^{VII} is extracted as pertechnetic acid according to equation (1.6).

$$H^+ + TcO_4^- + 3TBP \rightarrow [HTcO_4.3TBP] \quad (1.6)$$

Pruett (87) suggested that both TBP and its monohydrate may coordinate $HTcO_4$ to give the solvate structure shown in figure 1.8. The fourth oxygen atom is coordinated by TBP in concentrated TBP solution or in the absence of nitric acid (88).

The level of solvent extraction of pertechnetate is massively increased when certain transition or actinide metal cations are

Figure 1.8 : Postulated Solvate Structure of the TBP-TcO_4^- Complex.


OP(OBu)3
H
O
Tc
O
O
O
H—O
H
H
O
H
OP(OBu)3
OP(OBu)3

present in the system. For example, potassium pertechnetate is virtually inextractable from 0.01 M HNO_3 solution into a 30% solution of TBP in CCl_4 (D_{Tc} < 0.0001). When 0.2 M U^{VI}, Th^{IV} or Zr^{IV} is added to the initial aqueous phase D_{Tc} is increased to values > 1 (86).

The enhancing effect of uranium on the extraction of pertechnetate is well-known (89-91) and is attributed to the pertechnetate anion replacing a nitrate ion in the uranium-TBP complex (equation 1.7).

$$[UO_2(NO_3)_2.2TBP] + TcO_4^- \rightarrow [UO_2(NO_3)(TcO_4).2TBP] + NO_3^- \quad (1.7)$$

There seems to be some disagreement as to the exact mechanism of extraction of the pertechnetate into the organic phase.

Macasek (84) considered the uranyl-nitrate-TBP complex as being a more effective extractor for TcO_4^- than the TBP itself and regards equation (1.7) as the mechanism of coextraction. Some workers however consider that the mixed uranyl-nitrate-TBP and uranyl-pertechnetate-nitrate-TBP complexes form simultaneously from the ions and are extracted (92, ref. 6; 93, ref. 17).

The addition of zirconium to these systems has been shown to further increase the coextraction of Tc^{VII} due to the production of both uranyl and zirconyl-nitrate pertechnetates. The extraction of pertechnetate under reprocessing conditions is enhanced by several fission product elements, of which zirconium is the most important. This enhancement is in fact mutual.

It is possible that the coextracted pertechnetate undergoes a two-stage process in which pertechnetate is initially extracted as a mixed zirconyl-nitrate-pertechnetate-TBP species via equation (1.8).

$$Zr^{4+} + TcO_4^- + 3NO_3^- + TBP \rightarrow [Zr(NO_3)_3(TcO_4).TBP] \quad (1.9)$$

This complex then dissociates in the organic phase, the technetium

remaining in the solvent owing to a ligand exchange reaction with a nitrate ion from the uranyl-nitrate-TBP complex.

The extraction of Zr^{IV} itself is weak and occurs slowly and if the contact time of the two phases is decreased sufficiently then the amount of extracted zirconium (and hence technetium) is decreased. Under counter current conditions, zirconium will probably accumulate around the active feed stage through recycling; this will result in a markedly higher extraction of technetium (27).

1.5 The Behaviour of Hydrazine as a Reductant

Hydrazine can act as a one-electron or two-electron reductant depending on the metal ion being reduced and its oxidation state, for instance, Fe^{III} undergoes a single-electron reduction to Fe^{II} (equations 1.10-12), whilst Cr^{VI} undergoes a two-electron reduction to Cr^{IV} (equations 1.13-15) (modified from ref. 94, p. 275-6)

$$Fe^{III} + N_2H_4 \rightarrow Fe^{II} + N_2H_3^{\cdot} + H^{+} \qquad (1.10)$$

$$2N_2H_3^{\cdot} \rightarrow N_4H_6 \qquad (1.11)$$

$$N_4H_6 \rightarrow N_2 + 2NH_3 \qquad (1.12)$$

$$Cr^{VI} + N_2H_4 \rightarrow Cr^{IV} + N_2H_2 + 2H^{+} \qquad (1.13)$$

$$2N_2H_2 \rightarrow N_4H_4 \qquad (1.14)$$

$$N_4H_4 \rightarrow N_2 + N_2H_4 \quad / \quad \rightarrow NH_3 + HN_3 \qquad (1.15)$$

It can be seen from the equations that it is possible to determine whether one or two-electron reduction is occurring by the nature of the hydrazine degradation products. However, the above scheme may not be complete and the products do vary depending on the acidity of the solution and the transition metal, so that one-electron reduction can produce only nitrogen and two-electron reduction can produce both ammonia and hydrazoic acid. A study of the mechanism

of the oxidation of hydrazine in aqueous solutions was carried out by Cahn and Powell (95) and Bottomley (96).

In the hope of understanding better the reactions between hydrazine and technetium, reactions with other metal ions have been briefly reviewed.

1.5.1 The oxidation of hydrazine by iron(III)

The oxidation of hydrazine by metal ions has been examined by many investigators (95, 97, 98). Higginson and Wright (97) in a classical paper examined the oxidation of hydrazine by iron(III) in acidic solution and proposed the following reaction scheme:

$$Fe^{III} + N_2H_4 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Fe^{II} + N_2H_3\cdot + H^+$$

$$2N_2H_3\cdot \xrightarrow{k_2} N_4H_6$$

$$N_4H_6 \xrightarrow{fast} 2NH_3 + N_2$$

$$2N_2H_3\cdot \xrightarrow{k_3} N_2H_4 + N_2H_2$$

$$N_2H_2 \xrightarrow[fast]{-2e} N_2 + 2H^+$$

$$Fe^{III} + N_2H_3\cdot \longrightarrow N_2H_2 + Fe^{II} + H^+$$

Cahn and Powell (95) also investigated the reaction of iron(III) with hydrazine and proposed a similar reaction scheme to that of Higginson and Wright, with the exception of their omission of the back reaction (k_{-1}).

1.5.2 The oxidation of hydrazine by chromium(VI)

The kinetics of the oxidation of hydrazine by the chromate ion have been studied both in homogeneous (99, 100) and heterogeneous (101) systems. Beck and Durham (99) proposed the following reaction scheme by analogy with the initial reaction step between

chromium(VI) and the bisulphite ion (102) which proceeds via a chromate–bisulphite anhydride.

$$HCrO_4^- + H^+ + HOSO_2^- \rightleftharpoons [O_3CrOSO_2H]^- + H_2O$$

They assumed that the first step in the chromium(VI)–hydrazine reaction is analogous to that above; the proposed reaction scheme is given below:

$$CrO_4^- + 2H^+ + H_2NNH_2 \underset{\text{fast}}{\overset{k_1}{\rightleftharpoons}} H_3\overset{+}{N}NH\cdot CrO_3H + H_2O$$

$$H_3\overset{+}{N}NH\cdot CrO_3H \xrightarrow[\text{slow}]{k_a} Cr^{IV} + N_2H_2 + H^+$$

$$H_3\overset{+}{N}NH\cdot CrO_3H + HCrO_4^- \underset{\text{fast}}{\overset{k_2}{\rightleftharpoons}} HO_3Cr\cdot NHNH\cdot CrO_3^- + H_2O + H^+$$

$$HO_3Cr\cdot NHNH\cdot CrO_3^- \xrightarrow{k_b} 2Cr^{IV} + N_2$$

$$2Cr^{IV} \rightleftharpoons Cr^V + Cr^{III}$$

$$Cr^{IV} + Cr^{VI} \rightleftharpoons 2Cr^V$$

$$H_2O_3CrO^- + H^+ + H_2\overset{+}{N}NH_3 \underset{\text{fast}}{\overset{k_3}{\rightleftharpoons}} H_2O_3Cr\overset{+}{N}HNH_3 + H_2O$$

$$H_2O_3Cr\cdot\overset{+}{N}HNH_3 \longrightarrow Cr^{III} + N_2H_2$$

$$2N_2H_2 + H^+ \longrightarrow N_2 + N_2H_5^+$$

Haight et al. (100) also studied this system and arrived at essentially the same reaction scheme except that they thought unlikely the formation of a chromium(VI) dimer linked by a bridging N_2H_2 molecule. Baumgartner et al. (101) who studied the heterogeneous oxidation of hydrazine by barium chromate concluded that neighbouring Cr^{VI} centres may play an active role in the breakdown of the complex in a way similar to that proposed by Beck and Durham (99) for homogeneous systems.

1.6 The Technetium-Catalysed Oxidation of Hydrazine

In all the previously mentioned systems, the oxidation of hydrazine has been carried out in the absence of species that reoxidise the reduced forms of the metal ions. If this were indeed to be the case, a cycle would be formed in which the metal would function as a catalyst and the so-called technetium-hydrazine reaction, which is essentially the technetium-catalysed oxidation of hydrazine by nitric or perchloric acids is such a system. This is a complex multi-step reaction in which the technetium, originally present as Tc^{VII}, is reduced by hydrazine to lower oxidation states, possibly as far as Tc^{III} (2). These species are then reoxidised by nitrate or perchlorate ions, thus enabling them to react with more hydrazine. This system has been studied in several of the countries which carry out a nuclear power programme and is of considerable significance in the reprocessing of irradiated nuclear fuel (2,9,15,16).

The practical importance of the reaction is that considerable quantities of hydrazine may be consumed, thus (a) leaving perhaps insufficient to scavenge nitrite effectively, and (b) producing excessive amounts of hydrazoic acid and ammonium salts.

The simplest approximation to the situation that occurs during the reprocessing of nuclear fuel is the direct reaction between technetium and hydrazine in a nitric acid medium. A more realistic study should also take into account the presence of uranium and plutonium, but such reactions are prohibitively complex although a variety of mechanisms have been proposed for them. The following tables summarise the schemes proposed by various workers to explain the observed kinetics of these systems (tables 1.2-1.4).

The mechanisms proposed are divergent, with varying ideas about the initiation reaction. Most groups seem to agree that the Tc^{VII} is

TABLE 12

Reaction Schemes proposed for the Technetium-Catalysed Oxidation of Hydrazine by Nitric Acid in the Presence of Uranium and Plutonium Ions

REACTION SCHEME	RATE OF REACTION	AUTHOR
$TcO_4^- + N_2H_5^+ \rightarrow Tc(X)^a \rightarrow Tc(V) + N_2$		
$TcO_4^- \xrightarrow{N_2H_5^+} Tc(VI)$	slow	
$Tc(VI) + NO_3^- \rightarrow Tc(VII) + NO_2^-$	fast	
$2\ Tc(VI) \rightarrow Tc(VII) + Tc(V)$	fast	Spitsyn (16)
$2\ Tc(V) \rightarrow Tc(VI) + Tc(IV)$	slow	
$Tc(V) \xrightarrow{N_2H_5^+/H^+} Tc(IV)$	moderately fast	
$TcO_4^- + 6H^+ \rightarrow TcO^{5+} + 3H_2O$	fast	Borovinskii (104)
$TcO^{5+} + Pu(III) \xrightarrow{H_2O_2} Pu(IV) + Tc(VI)$		
$Tc(VI) + HNO_3 + 3H^+ \rightarrow TcO_4^- + NO + 2H_2O$		

[a] = Tc(X) is probably a Tc(V) complex of hydrazine or a hydrazine degradation product

TABLE 13

Reaction Schemes proposed for the Technetium-Catalysed Oxidation of Hydrazine by Nitric Acid in the presence of Uranium and Plutonium Ions (Modified from Ref. 89)

Reaction Scheme	Rate of Reaction / mol dm^{-3} s^{-1}	Author
$TcO_4^- + xe \xrightarrow{N_2H_5^+} Tc(7-x)$	fast	Vialard (102)
$TcO_4^- + xe \xrightarrow{U(IV)} Tc(7-x)$	fast	
$Tc(7-x) \xrightarrow{NO_3^-} TcO_4^- + xe$		
$Tc(VII) + e \xrightarrow{N_2H_5^+} Tc(VI)$		Akopov (103)
$Tc(VI) + e \xrightarrow{N_2H_5^+} Tc(V)$		
$Tc(V) \xrightarrow{NO_3^-} Tc(VI)$		
$Tc(VI) \xrightarrow{NO_3^-} Tc(VII)$		
$N_3^- \xrightarrow{NO_2^-} N_2$		
$Tc(VII) + N_2H_5^+ \rightarrow \frac{[Tc(VI)]}{[Tc(V)]} \rightarrow Tc(IV)$		Koltunov (9)
$Tc(V) + NO_3^- \rightarrow Tc(VII) + NO_2^-$	0.32 ± 0.02 at 25°C	
$Tc(IV) + NO_3^- \rightarrow Tc(VII) + NO$	v. slow	
$3\ Tc(V) \rightarrow Tc(VII) + 2Tc(IV)$	fast	
$3\ Tc(VI) \rightarrow 2Tc(VII) + Tc(IV)$	v. fast	
$Tc(VII) \xrightarrow{U(IV)} Tc(IV)$	moderately fast	
$Tc(VII) + U(IV) \rightarrow Tc(V) + UO_2^{2+}$	slow	
$Pu(III) + Tc(VII) \rightarrow Pu(IV) + Tc(VI)$		
$2Pu(III) + U(IV) \rightarrow 2Pu(IV) + U(VI)$		

TABLE 14

Reaction Scheme proposed for the Technetium-Catalysed Oxidation of Hydrazine by Nitric Acid in the Presence of Uranium and Plutonium Ions
Garraway and Wilson (15,27)

Reaction Scheme	Rate of Reaction/mol dm^{-3} s^{-1}
$TcO_4^- \xrightarrow{HNO_3} TcO_3^+$	slow
$TcO_3^+ \xrightarrow{H^+} TcO_4^-$	slow
$TcO_3^+ + N_2H_5^+ \rightarrow$ Tc(VI)	fast
$Tc(V) + N_2H_5^+ \rightarrow$ Tc(IV)	0.208
$Tc(IV) + TcO_4^- \rightarrow$ Tc(VI) + Tc(V)	2.778
$Tc(IV) + NO_3^- \rightarrow$ Tc(VI) + NO_2^-	0.008
$Tc(VI) + N_2H_5^+ \rightarrow$ Tc(IV)	0.208
$Tc(VI) + NO_3^- \rightarrow TcO_4^- + NO_2^-$	5.6×10^{-4}
$Tc(VI) + NO_3^- \rightarrow TcO_4^- + NO_2^-$	0..003
$NO_2^- + N_2H_5^+ \rightarrow HN_3 + 2H_2O$	0.139
$HN_3 + N_2H_3^+ \rightarrow NH_4^+ + 2N_2$	slow
$NO_2^- + N_3^- \rightarrow N_2O + N_2 + H_2O$	v. slow
$TcO_4^- + 3e \xrightarrow{U(IV)}$ Tc(IV)	fast
$Tc(VI) + U(IV) \rightarrow Tc(IV) + U(VI)$	fast
$Tc(VI) + Pu(IV) \rightarrow TcO_4^- + Pu(III)$	v. fast
$Tc(V) + Pu(IV) \rightarrow Tc(VI) + Pu(III)$	fast
$Tc(IV) + Pu(IV) \rightarrow Tc(V) + Pu(III)$	v. fast (> 2.8)
$Pu(III) + NO_2^- \rightarrow Pu(IV) + NO_2$	fast (< 0.14)

reduced by hydrazine in a single-electron step to Tc^{VI}, followed by further reduction. Spitsyn et al. (16) however proposed the direct two-electron reduction of Tc^{VII} to Tc^{V}.

It is also generally agreed that the reduction of Tc^{VII} by hydrazine continues until Tc^{IV} is reached. Koltunov et al. (9) proposed that the final reduction product in the hydrazine oxidation is Tc^{V}, any Tc^{IV} being produced due to Tc^{V} disproportionating. It has also been postulated that some of the technetium could be reduced as far as Tc^{III}. Zelverte (2) followed the electrochemical reduction of pertechnetate in water by U.V-vis. spectroscopy and obtained spectra for the oxidation states + 5, +4 and +3. However, spectra of technetium-hydrazine reaction mixtures followed by U.V-vis spectroscopy did not show any peaks attributable to Tc^{III}. This absence of peaks could be due to the very rapid oxidation of Tc^{III} to Tc^{IV} by nitrate ion, leading to only traces of Tc^{III} being present. Tc^{VI} in aqueous solution is similarly highly reactive judging from pulse radiolysis studies and is present in the reaction system only as a transient intermediate.

The lack of agreement concerning the nature and oxidation state of the Tc-hydrazine products also extends to the postulated reactions involving technetium intermediates and uranium or plutonium ions. Koltunov et al. (9) and Borovinskii et al. (104) reported the oxidation of Pu^{III} by TcO_4^- at elevated temperatures and acidities. However this is unlikely as Garraway and Wilson pointed out (27), as the reverse reaction is rapid. Such a reaction step would decrease the length of the induction period of the TcO_4^--hydrazine reaction which is contrary to their experimental data (27); moreover the literature data indicate that the reaction is endothermic (105,106) and therefore less significant at the lower temperatures that are of

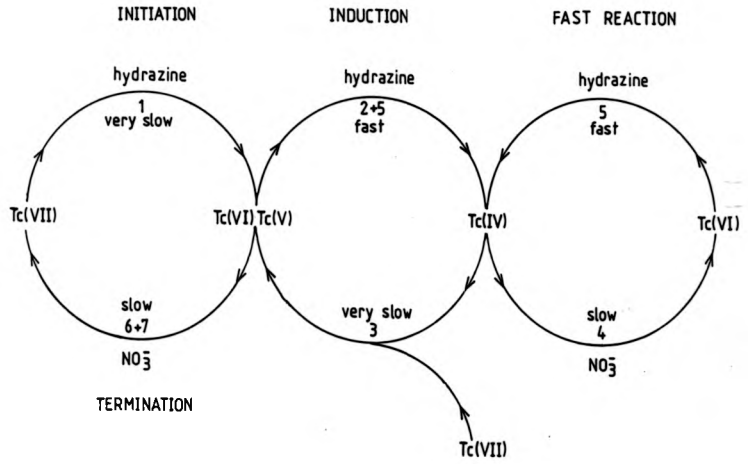
technological interest. It is more probable that the oxidation of Pu^{III} observed by the Russians was due to its reaction with nitrite which would be present in significant amounts.

The most detailed and comprehensive study that has been carried out into this reaction was conducted by Garraway et al. (15,27). The reaction scheme proposed by them is exceedingly complex (Table 1.3), but the basic system involving solely TcO_4^--hydrazine and nitrate ion as initial reactants has been qualitatively simulated by them using a purpose-written computer program. One aspect of the work of this thesis has been to extend this computer simulation to take into account the marked effect of acidity and the presence of uranium and plutonium ions.

The destruction of hydrazine in the so called technetium-hydrazine reaction displays three main features, an induction period, a fast reaction and a termination stage. In modelling the whole course of reaction, Garraway and Wilson have suggested individual reaction steps that occur during each of these stages and have derived mutually consistent rate constants for them. The reactions that occur in the basic Tc-N_2H_4 system can best be visualised from the cyclic diagram presented as figure 1.9 (from ref. 15).

The reaction displays an induction period which comprises an initial slow reduction of Tc^{VII} by hydrazine to give Tc^{VI} and Tc^{V} (the initiation stage), followed by the faster reduction of these species to Tc^{IV} by hydrazine (the induction stage). The fast reaction commences when Tc^{VII} has been substantially reduced to Tc^{IV}. At each stage in the reaction scheme, lower oxidation states of Tc are oxidised by nitrate, the termination reaction being the acid-catalysed oxidation of Tc^{VI} by nitrate when reduction by hydrazine can no longer complete effectively. Under most conditions

Figure 1.9 : Reaction Scheme proposed by Garraway and Wilson (15) for the Reaction between Tc-Hydrazine and Nitric Acid.


INITIATION
INDUCTION
FAST REACTION
hydrazine
1
very slow
hydrazine
2+5
fast
hydrazine
5
fast
Tc(VII)
Tc(VI)
Tc(V)
Tc(IV)
Tc(VI)
slow
6+7
NO_3^-
very slow
3
slow
4
NO_3^-
TERMINATION
Tc(VII)

a residual plateau concentration of hydrazine remains. On completion of the reaction all the technetium is present as Tc^{VII} except at elevated hydrazine or nitrate concentrations; TcO_4^- therefore functions as a true catalyst, featuring a high turnover number and quantitative regeneration. The major degradation products of hydrazine are ammonia, azide ion and nitrogen.

1.7 Objects of the Present Work

(i) To test more fully the model derived by Garraway and Wilson, it was proposed to examine in detail:

(a) the effect of acidity in a nitrate medium over a fuller range.

(b) the specific effects of NO_3^- ion on the rates of the individual steps.

(c) to model the effects of added Pu^{III} or Pu^{IV} and U^{IV}.

Operation in a nitric acid-nitrate ion medium had the disadvantages that:

(a) nitrate or acid concentration could not be varied while maintaining a constant ionic strength.

(b) the effect of varying nitrate ion concentration could not be separated from the effects of acidity and

(c) it interfered with the spectrophotometric monitoring of the pertechnetate ion.

(ii) An attempt was therefore made to overcome these difficulties by working in a perchlorate medium, in the reasonable expectation that perchlorate ion would be inert. However, it proved to be a highly effective oxidant in this system, with both similarities to and differences from nitrate ion: this has generated a further study on its own

account, detailed in a separate section of this thesis.

(iii) Alternatives that might be genuinely inert and usable to maintain a constant ionic strength were trifluoroacetic and tetrafluoroboric acids. Hydrochloric acid was also employed but this resulted in the production of chloro-complexes of the reduced technetium species.

Trifluoroacetate, like nitrate, interfered with spectrophotometric assay, but tetrafluoroborate did not and some useful results have been obtained from this system.

(iv) A study was also made of the residual pink or yellow coloured solutions from the TcO_4^--N_2H_4-NO_3^- reaction reported by Garraway and Wilson using e.s.r. spectroscopy at 77 and 298 K. This was extended to include studies in perchlorate, trifluoroacetate and sodium hydroxide media.

2. Kinetics of the TcO_4^--Hydrazine Reaction in Nitrate-Containing Media

We have carried out investigations in nitric acid systems using colorimetric assays of sample aliquots to monitor changing hydrazine and Tc^{IV} and Tc^{V} concentrations (see Experimental Section).

Investigations into the effects of changing the concentrations of nitric acid, nitrate ion and technetium have also been carried out ; some of these results have been reproduced using computer simulation.

It was decided not to follow the changing concentration of Tc^{IV} or Tc^{V} as the effects of these species on the rate of reaction had already been fully investigated by Eggleton and Wilson (112) and Garraway and Wilson (15,27).

The so-called technetium-hydrazine reaction is the technetium-catalysed oxidation of hydrazine by the nitrate ion in acid solution. The reaction can be conveniently regarded as divided into three stages which are apparent from the hydrazine oxidation profile.

After initiating the reaction, for instance, by adding hydrazine, a time lag of varying length, from minutes to hours, occurs depending on the reaction conditions. This interval is referred to as the induction period and covers the initial slow reduction of TcO_4^- to Tc^{VI} by hydrazine, followed by a rapid comproportionation reaction between Tc^{IV} and TcO_4^- to yield Tc^{V} and Tc^{VI}. The next stage, the so-called "fast reaction" stage, commences when TcO_4^- has been substantially reduced to Tc^{IV}. The mechanism of the fast reaction is considered to be the reduction of Tc^{VI} to Tc^{IV} by hydrazine followed by the slow oxidation of Tc^{IV} back to Tc^{VI} by NO_3^-; this

results in a very rapid loss of hydrazine from the solution. The final stage, referred to as the termination stage, is entered at elevated (> 4 mol dm^{-3}) nitric acid concentrations or when the hydrazine concentration has been substantially reduced. The termination reaction consists of the acid-catalysed oxidation of Tc^{VI} to TcO_4^- by nitrate ion.

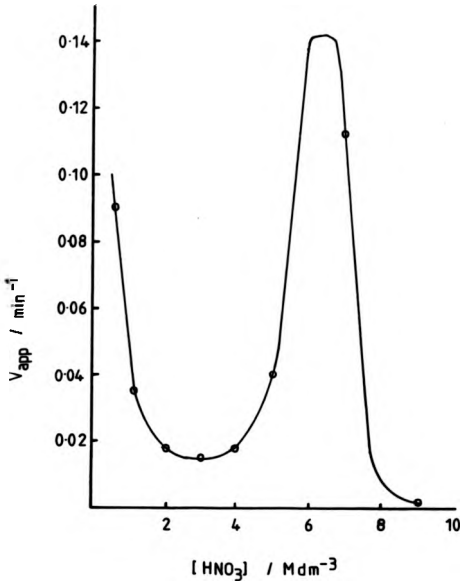
A more detailed account of this reaction scheme is given in the Introduction, Section 1, along with a figure illustrating the proposed reaction scheme (Figure 1.9).

2.1 Effect of Nitric Acid Concentration

The effect of changes in the concentration of nitric acid is known to be complex. Garraway and Wilson (15) found that increase in nitric acid concentration up to about 3 mol dm^{-3} accelerated both the induction reaction and the fast reaction. At higher concentrations, however, they found in addition a marked inhibitory effect, causing the reaction to terminate with increasing residual concentrations of hydrazine until there is essentially zero consumption of hydrazine at acidities of 6 mol dm^{-3} or higher.

Spitsyn et al. (16) followed the course of the reaction in nitric and perchloric acids by monitoring the changing absorbance of the solution at 500 nm. They attributed the development of this absorbance to the formation of a Tc^{V} species. By plotting the absorbance at 500 nm versus time, they obtained an S-shape curve; at temperatures above 40°C they observed that some curves became two-stage and attributed the second stage to the reduction of Tc^{V} to Tc^{IV}. By plotting the apparent rate of pertechnetate reduction V_{app} versus $[HNO_3]$ they obtained the shape depicted in Figure 2.1. It can be seen that the rate of pertechnetate reduction displays two maxima, one below 1.0 mol dm^{-3} HNO_3 which they attributed to the

Figure 2.1 : Apparent Rate of TcO_4^- Reduction Versus Nitric Acid Concentration (16) at High Hydrazine Concentrations (based on changes in λ_{max} 500 nm)


0·14
0·12
0·10
0·08
0·06
0·04
0·02
V_{app} / min^{-1}
2
4
6
8
10
[HNO_3] / Mdm^{-3}

precipitation of hydrated Tc^{IV} or Tc^{V} oxides and the other at 6 mol dm^{-3} HNO_3. The latter observation is contrary to our general observations as we found the development of colour in the reaction mixtures to decrease with increasing acidity. At 6 mol dm^{-3} HNO_3 no colour was observed to form and only traces of Tc^{IV} and Tc^{V} were detected. There are several explanations for this difference. The Russians used far higher concentrations of technetium and hydrazine than ourselves, so it is quite possible that at these concentrations the reaction would proceed even in moderately concentrated (> 6 mol dm^{-3}) nitric acid. Indeed they report that the reaction proceeded even in concentrated nitric acid, assuming an explosive character (with $[N_2H_4] > 1$ mol dm^{-3} and $[Tc] > 6 \times 10^{-3}$ mol dm^{-3}). Presumably there is a critical ratio of Tc : N_2H_4 : HNO_3 above which no reaction will occur at high acid concentrations due to the rate of reduction of pertechnetate exceeding the rate of its reformation.
An alternative explanation could lie in the fact that the Russians also added Fe^{2+} to their system, which could initiate additional reactions; their report of a coloration with λ_{max} ca. 450 nm, which they attributed to the production of Tc^{V}, could equally well be due to an Fe^{III}-azide complex which would be produced in appreciable concentrations.

2.1.1 Effect of Nitric Acid at $[Tc] = 7.2 \times 10^{-4}$ mol dm^{-3}

The selection of this concentration of Tc for the first series of experiments was prompted by (i) the need to conserve this expensive material, (ii) to reduce risks due to spillage, (iii) to reduce the problem of disposal. Experience showed that a somewhat higher concentration offered greater benefits in terms of reaction times, degrees of conversion, sensitivity of Tc towards analysis,

etc., which more than offset the disadvantages mentioned above.

However, the experiments at very low [Tc] provide useful confirmation of the much larger series carried out at higher [Tc], and are therefore briefly described here. The nitrate ion concentration in these reactions was maintained between 7.33 and 7.86 mol dm^{-3} by adding sodium nitrate. In this concentration range, considerable difficulty was experienced in dissolving the sodium nitrate, particularly at the lower acid concentrations. In the light of experience, when a higher Tc concentration was used the total nitrate ion concentration was reduced to 7.0 mol dm^{-3}.

The effects of increasing the concentration of nitric acid at constant nitrate ion concentration on the destruction of hydrazine are shown in Figures 2.2 and 2.3. In Figure 2.4 the rate of the fast reaction is plotted against nitric acid concentration.

Increasing the acidity increases the residual concentration of hydrazine and decreases the rate of the fast reaction to such an extent that at 6.8 mol dm^{-3} nitric acid there was only ca. 6 ± 2 per cent destruction of hydrazine after 24 hours. At 7.9 mol dm^{-3} nitric acid a very low degree of destruction of hydrazine was again observed, i.e. ca. 9 ± 5 per cent.

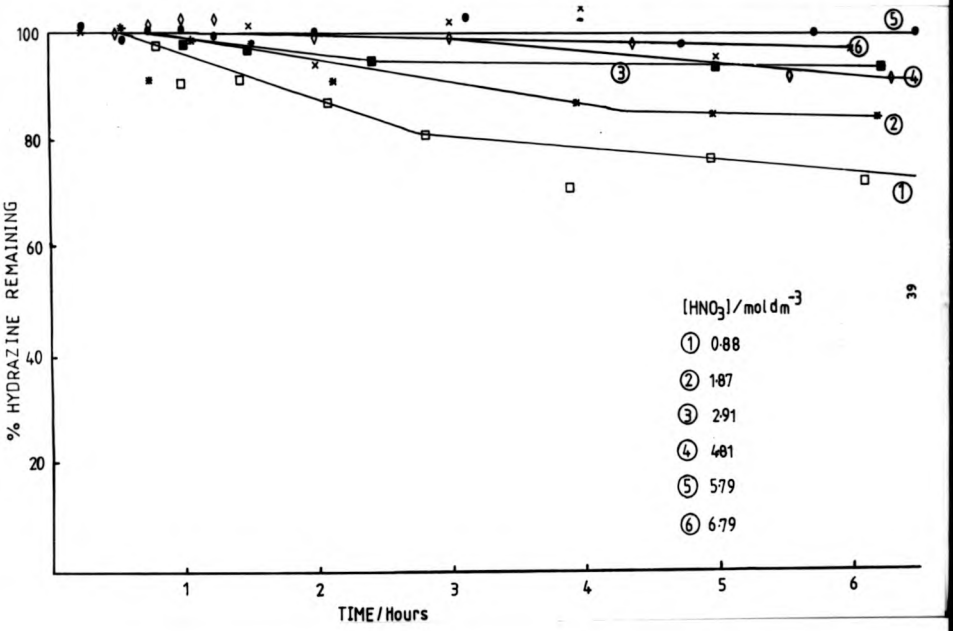
It seemed possible that this small apparent increase in hydrazine destruction was due to the oxidation of hydrazine by nitric acid itself. However, we observed no such oxidation in a technetium-free 7 mol dm^{-3} nitric acid solution; even so in 16 mol dm^{-3} acid however, almost complete destruction was observed.

Time-Dependence of the Destruction of Hydrazine at Varying Nitric Acid Concentrations (Low [Tc] Series)

[Tc]	:	7.15×10^{-4} M (as TcO_4^- initially)
$[N_2H_5NO_3]$	:	0.1 M
$[NO_3^-]_{Total}$	:	7.33 - 7.36 M
Temp.	:	35°C

Figure 2.2 : Destruction of Hydrazine over the First Six Hours of Reaction

Figure 2.3 : Destruction of Hydrazine over a 26 Hour Period


100
80
60
40
20
% HYDRAZINE REMAINING
1
2
3
4
5
6
TIME / Hours
[HNO3] / mol dm-3
① 0·88
② 1·87
③ 2·91
④ 4·81
⑤ 5·79
⑥ 6·79
39

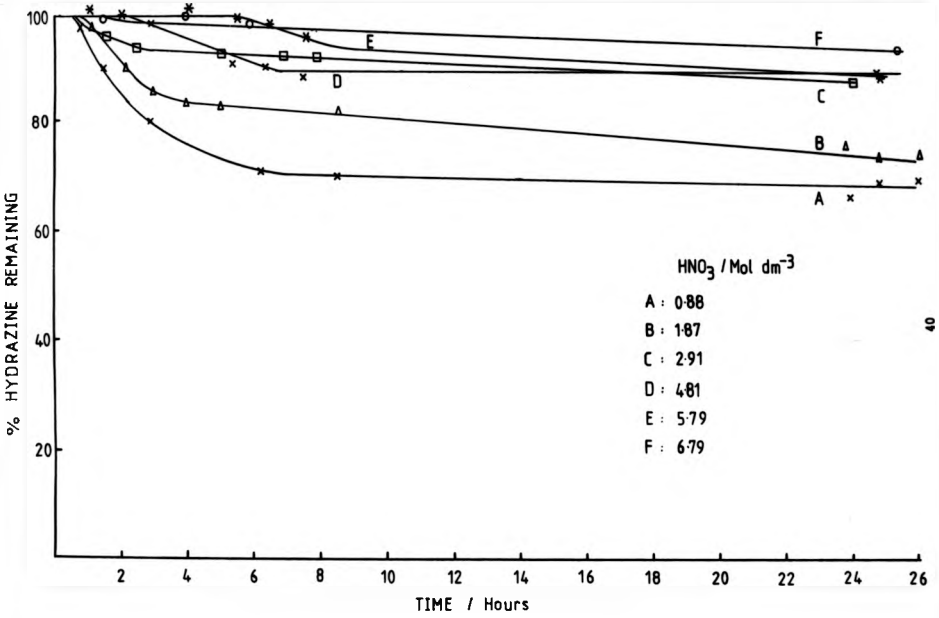
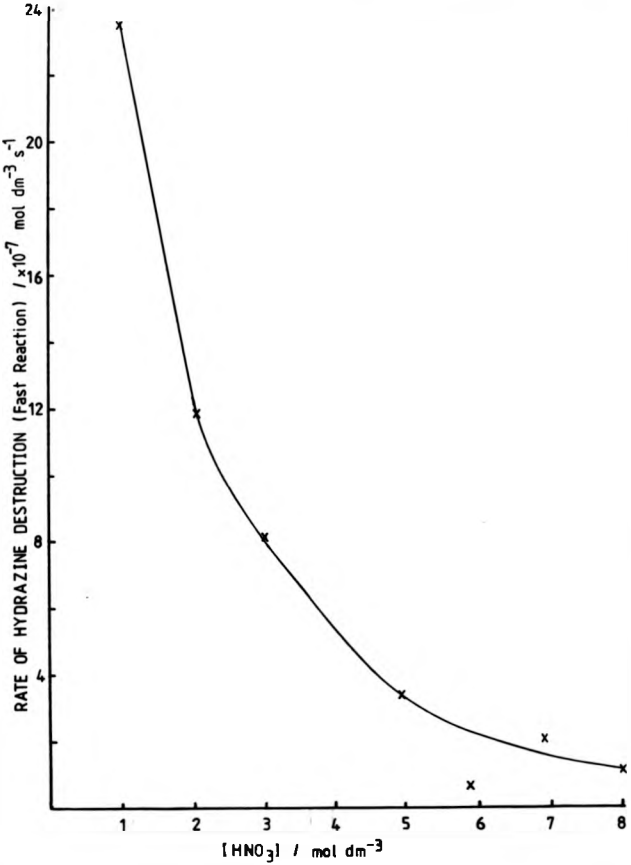

% HYDRAZINE REMAINING
100
80
60
40
20
2
4
6
8
10
12
14
16
18
20
22
24
26
TIME / Hours
A
B
C
D
E
F
HNO3 / Mol dm-3
A : 0·88
B : 1·87
C : 2·91
D : 4·81
E : 5·79
F : 6·79

Figure 2.4 : Rate of Destruction of Hydrazine (During Fast Reaction) with Varying Nitric Acid Concentration (Low [Tc] Series).

[Tc]	:	7.15×10^{-4} M (as TcO_4^- initially)
$[N_2H_5NO_3]$	:	0.1 M
$[HNO_3]$	:	Varied
$[NO_3^-]_{Total}$	:	7.33 - 7.86 M
Temp	:	35^oC


RATE OF HYDRAZINE DESTRUCTION (Fast Reaction) / $\times 10^{-7}$ mol dm^{-3} s^{-1}
24
20
16
12
8
4
1
2
3
4
5
6
7
8
[HNO$_3$] / mol dm^{-3}

2.1.2 Effect of Nitric Acid at [Tc] = 1.6×10^{-3} mol dm^{-3}

In order to establish whether the low level of hydrazine oxidation (< 30%) was due either to the low Tc concentration (7.2×10^{-4} mol dm^{-3} initially chosen) or to inhibition by the high nitrate ion concentration, a reaction was carried out in 4 mol dm^{-3} nitric acid (total $[NO_3^-]$ = 4 mol dm^{-3} using $[TcO_4^-]$ = 7.2×10^{-4} mol dm^{-3}). This reaction led to a greater (39%) destruction of hydrazine after 24 hours, indicating that it would indeed be feasible to use the low Tc concentration provided one worked at or below this relatively low acidity. However, since the object of this study was to investigate the reaction kinetics over a wide range of nitric acid concentrations (0.1 - 7.0 mol dm^{-3}), a high nitrate ion concentration (7.0 mol dm^{-3}) was required in order to ensure a constant oxidant concentration (the nitrate ion) and ionic strength.

It was decided to overcome the problems of slow kinetics which result from employing a high nitrate concentration by raising the concentration of technetium. The advantages of this are twofold:

(a) the oxidation of hydrazine during the fast reaction stage takes place faster, resulting in a lower residual concentration of unreacted hydrazine and

(b) since the technetium concentration in the IBX column of THORP, where the reductive separation of plutonium from uranium occurs, is expected to be ca. 1.3×10^{-3} mol dm^{-3}, we decided to conduct all subsequent studies with [Tc] maintained at 1.6×10^{-3} mol dm^{-3} to simulate better the conditions expected in the IBX column of THORP.

This kinetic study, like that conducted with the lower Tc concentration, indicates that increase in acidity leads to lengthening of the initiation period and reduction in the final

level of destruction of hydrazine, i.e. the oxidation is inhibited at higher acid concentrations.

Acid concentrations ranging from 0.1 to 7.0 mol dm^{-3} were utilised and the results are illustrated in Figures 2.5 and 2.6. The percentage of hydrazine destroyed increased with decreasing acidity until at 0.5 mol dm^{-3} there was a 40 ± 3% loss at 8 hours; however lowering the acidity still further to 0.1 mol dm^{-3} only resulted in 48 ± 3 per cent destruction at 8 hours.

In Figure 2.7 the rate of the fast reaction is plotted against nitric acid concentration. At both technetium concentrations studied the rate of hydrazine oxidation increased with decreasing acidity, the reaction rate being a factor of 10 greater for the higher Tc concentration.

2.2.1 Study of the Acidity Dependence in a Tc-N_2H_4-0.6 M - $NaNO_3$-HBF_4 System

In order to elucidate more fully the mutual effects of nitric acid and nitrate ion on the reaction, nitric acid was replaced by tetrafluoroboric acid, the ionic strength being maintained (at μ = 5.1 mol dm^{-3}) by adding sodium tetrafluoroborate. (Hydrohalic acids could not be employed as their use would result in the formation of oxyhalo-technetium complexes which could have different reactivities from the simple hydrolysed oxo-technetium species thought to be produced in nitric acid.)

The effects of increasing the concentration of tetrafluoroboric acid on the oxidation of hydrazine, the production of ammonium ions and the evolution of Tc^{IV} and Tc^{V} were studied.

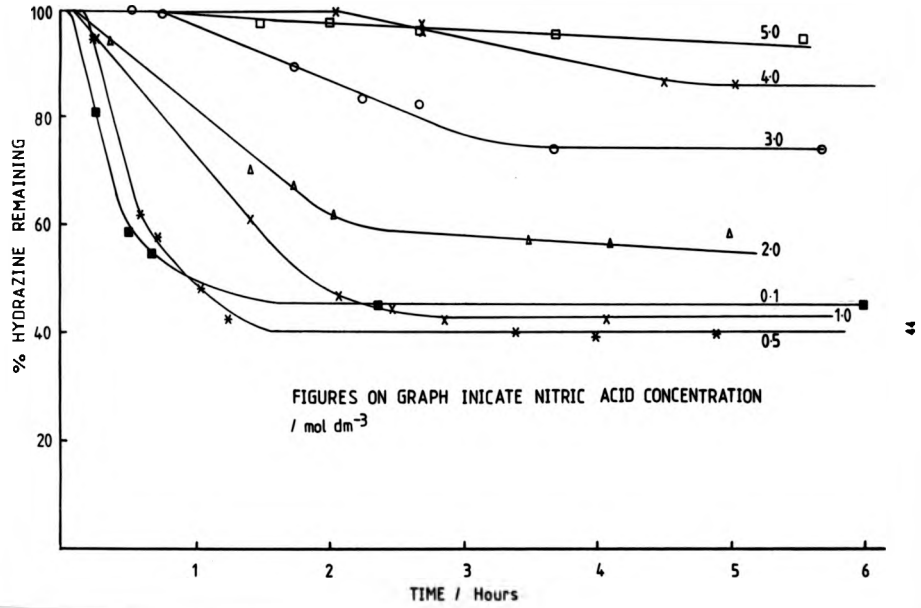
The reactions leading to the production of ammonium ions are complex. It is certain that some ammonia is produced directly during the oxidation of hydrazine, although substantial amounts are

Time-Dependence of the Destruction of Hydrazine at Varying Nitric Acid Concentrations (High [Tc] Series)

[Tc]	:	1.6×10^{-3} M (as TcO_4^- initially)
$[N_2H_5NO_3]$	:	0.1 M
$[NO_3^-]_{Total}$	:	7.0 M
Temp.	:	35°C

Figure 2.5 : Destruction of Hydrazine over the First 6 Hours

Figure 2.6 : Destruction of Hydrazine over a 26 Hour Period


100
80
60
40
20
% HYDRAZINE REMAINING
5·0
4·0
3·0
2·0
0·1
1·0
0·5
FIGURES ON GRAPH INICATE NITRIC ACID CONCENTRATION
/ mol dm⁻³
1
2
3
4
5
6
TIME / Hours

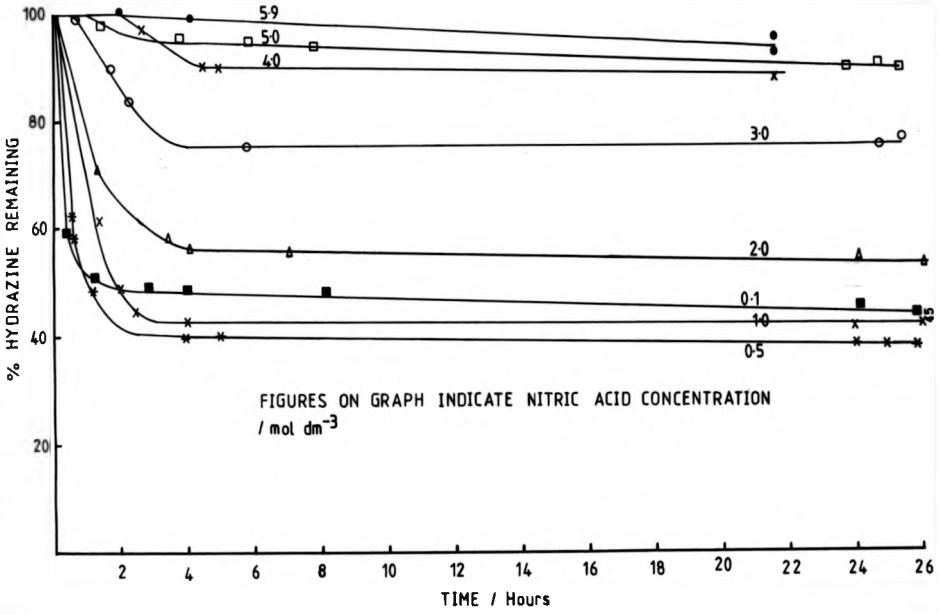
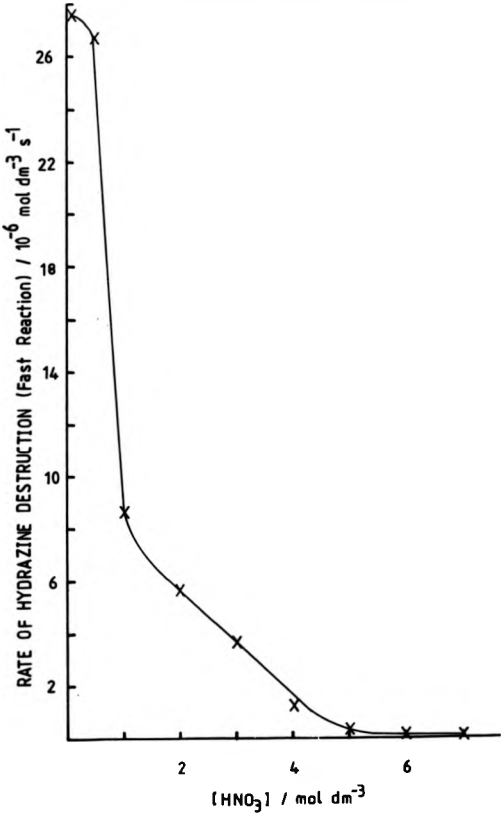

100
80
60
40
20
% HYDRAZINE REMAINING
5·9
5·0
4·0
3·0
2·0
0·1
1·0
0·5
FIGURES ON GRAPH INDICATE NITRIC ACID CONCENTRATION
/ mol dm⁻³
2
4
6
8
10
12
14
16
18
20
22
24
26
TIME / Hours

Figure 2.7 : Rate of Destruction of Hydrazine (During Fast Reaction Stage) with Varying Nitric Acid Concentration

[Tc]	:	1.6×10^{-3} M (as TcO_4^- initially)
$[N_2H_5NO_3]$	:	0.1 M
$[NO_3^-]_{Total}$	:	7.0 M
Temp.	:	35°C


RATE OF HYDRAZINE DESTRUCTION (Fast Reaction) / 10^{-6} mol dm^{-3} s^{-1}
26
22
18
14
10
6
2
2
4
6
[HNO_3] / mol dm^{-3}

also produced via the oxidation of hydrazoic acid, another major breakdown product of hydrazine.

The pathway followed will depend on the nature of the oxidising species, i.e. whether it will undergo 1-electron or 2-electron oxidation. Cahn and Powell (95) studied the oxidation of hydrazine using iron(III) as an oxidant, arriving at the following reaction scheme.

$$N_2H_5^+ \rightarrow 1e^- + N_2H_3 + 2H^+ \qquad [2.1]$$

$$2N_2H_3 \rightarrow NH_2 - NH - NH - NH_2 \qquad [2.2]$$

$$NH_2 - NH - NH - NH_2 \rightarrow NH_3 + HN = N - NH_2 \qquad [2.3]$$

$$N_3H_3 \rightarrow NH_3 + N_2$$

OR

$$NH_2 - NH - NH - NH_2 \rightarrow 2e^- + NH_3 + HN_3 + 2H^+ \qquad [2.4]$$

They also proposed that the N_3H_3 produced could react further with iron(III), giving N_2H_2, which would react as follows

$$2N_2H_2 \rightarrow N_4H_4 \qquad [2.5]$$

$$N_4H_4 \rightarrow N_2 + N_2H_4 \qquad [2.6]$$
$$N_4H_4 \rightarrow NH_3 + HN_3 \qquad [2.6]$$

The direct 2-electron oxidation of hydrazine would also lead to the production of N_2H_2; thus it is possible that equations [2.5] and [2.6] occur in the 'fast reaction stage' of the Tc-hydrazine reaction.

The hydrazoic acid produced would react via an undefined pathway, possibly involving a Tc^{VI}-nitride species as an intermediate

complex, to give nitrogen and ammonia.

The experimental results we obtained for the HBF_4- $NaNO_3$ system display several marked differences from the situation found in nitric acid alone. The effects of increasing acidity on the oxidation of hydrazine and the production of Tc^{IV} and Tc^{V} are shown in Figures 2.8 and 2.9. It can be seen that as the acidity is increased, the initiation period decreases and the rate of the fast reaction increases slightly. This increase in rate however is not as pronounced as the change in rate that occurs over the same acidity range in nitric acid.

The second major difference lies in the production of Tc^{IV}. The results obtained by Garraway and Wilson (15) for a nitric acid system show a single broad peak in the production of Tc^{IV} during the fast reaction stage. All the Tc^{IV} produced is re-oxidised back to Tc^{VII} during the termination stage.

In HBF_4-$NaNO_3$ media we observed that the concentration of Tc^{IV} reaches a peak (as is also the case with Tc^{V}), the Tc^{IV} is then rapidly oxidised, albeit leaving a residual 'plateau' concentration of about 15 per cent (of all Tc) for the remainder of the reaction. This peak in the production of Tc^{IV} or Tc^{V} occurs at all four acidities, the actual yield of Tc^{IV} or Tc^{V} falling with decreasing acid concentration. This decreasing 'peak' production of Tc^{IV} can be seen in Figure 2.10. It is interesting to note that the 'peak' concentration of Tc^{IV} can be correlated with the rate of the fast reaction, Figure 2.11.

The production of ammonium ions was also determined at each of the four acidities employed ; the yield of NH_4^+ decreases with increasing acidity as illustrated in Table 2.1.

Thus the production of ammonium ions is inhibited by acid. This

Figure 2.8 : Destruction of Hydrazine over Time at Varying Tetrafluoroboric Acid Concentrations

[Tc]	:	1.6×10^{-3} M
$[N_2H_5H_2O]$	:	0.1 M
$[NaNO_3]$	:	0.6 M
$[HNO_3]$	:	0.05 M
$[BF_4^-]_{Total}$	:	5.0 M
Temp.	:	35°C

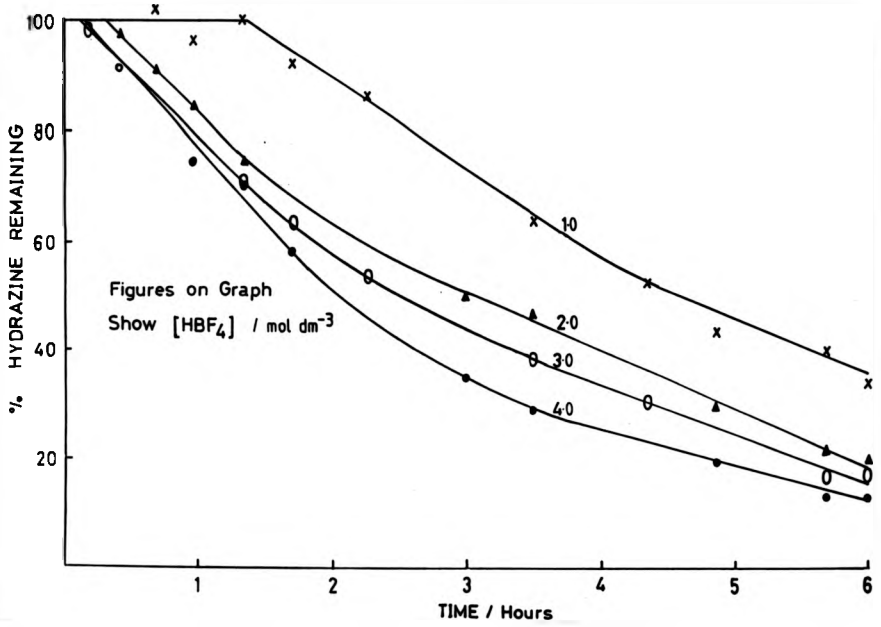

100
80
60
40
20
% HYDRAZINE REMAINING
Figures on Graph
Show [HBF4] / mol dm-3
1·0
2·0
3·0
4·0
1
2
3
4
5
6
TIME / Hours

Figure 2.9 : The Evolution of Tc^{IV} and Tc^{V} over Time with Varying Tetrafluoroboric Acid Concentration

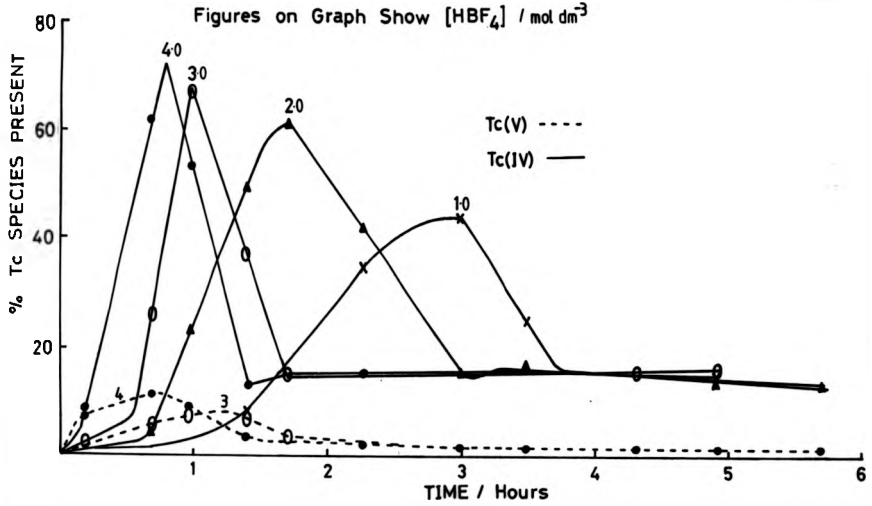
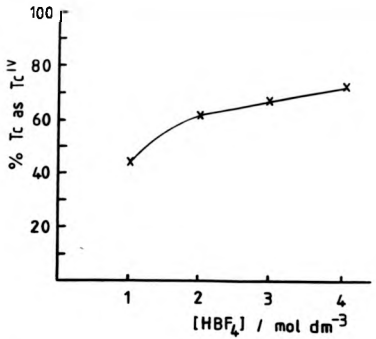

Figures on Graph Show [HBF4] / mol dm-3
4·0
3·0
2·0
1·0
Tc(V) ----
Tc(IV) ——
% Tc SPECIES PRESENT
TIME / Hours
80
60
40
20
1
2
3
4
5
6

Figure 2.10 : Peak Percentage Conversion of Tc to Tc^{IV} versus HBF_4 Concentration

Figure 2.11 : Correlation between the Rate of the Fast Reaction and the Tc^{IV} Concentration


100
80
60
40
20
% Tc as Tc IV
1
2
3
4
[HBF4] / mol dm-3

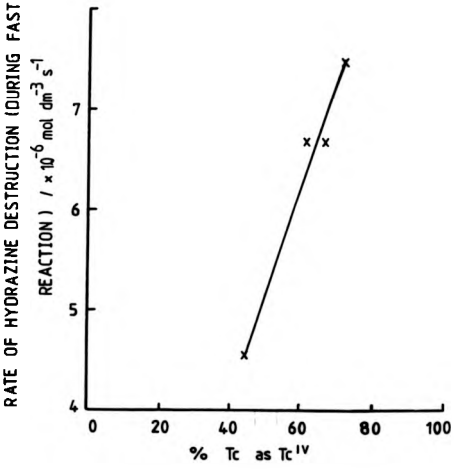

RATE OF HYDRAZINE DESTRUCTION (DURING FAST REACTION) / x 10-6 mol dm-3 s-1
7
6
5
4
0
20
40
60
80
100
% Tc as Tc IV

Table 2.1 : Variation in the Production of Ammonium Ions with Increasing Tetrafluoroboric Acid Concentration

$[HBF_4]$ /mol dm^{-3}	1.0	2.0	3.0	4.0
$[NH_4]^+$ Produced /mol dm^{-3}	0.0257	0.0262	0.0282	0.0249
$[N_2H_4]$ oxidised /mol dm^{-3}	0.0660	0.0813	0.0843	0.0873
Yield of NH_4^+ /mole % based on hydrazine loss	38.9	32.2	33.3	28.5

acid inhibition was also observed by Garraway and Wilson (15) who proposed that the acid dependent reaction was that between the nitrite ion and hydrazine. This very significant reaction can follow two pathways depending on the acidity, as follows (equations 2.7 and 2.8):

$$HNO_2 + N_2H_5^+ \rightarrow HN_3 + 2H_2O + H^+ \qquad [2.7]$$

$$\rightarrow NH_4^+ + N_2O + H_2O \qquad [2.8]$$

The relative rates of the reactions are acid-dependent, the ratio of the products being given by the following expression (15), equation 2.9.

$$\frac{[HN_3]}{[NH_4^+]} = 0.44 + 0.25\,[H^+] \qquad [2.9]$$

This work has been studied in depth both by Phelan (115) and Stedman et al. (116-118). Clearly the effect of acidity is to increase the production of azide at the expense of ammonia.

Another reaction probably leading to the production of ammonia is the Tc^{IV} or Tc^{V}-catalysed oxidation of azide to nitrogen and presumably ammonia. The reaction between Tc^{V} and azide has been investigated and will be dealt with in greater detail later, Section 6.1. In the presence of Tc^{V}, azide and hydrochloric acid, the reaction products are N_2 and a nitrido complex of Tc^{VI}. It is possible that in nitric acid a complex of Tc^{VI} may be produced that would subsequently be reduced back to Tc^{IV} or Tc^{V}, and hence catalysis by technetium would be observed.

2.2.2 Study of the Acidity Dependence in a Tc-N_2H_4-2.0 M $NaNO_3$-HBF_4 System

In the system previously detailed, Section 2.2.1, the acid was present in excess over nitrate ion in all four reaction mixtures. It was therefore decided to conduct a study in which the nitrate ion would be in excess over acid for at least some of the

reactions.

As in the study of the 0.6 mol dm^{-3} $NaNO_3$ system, the reaction mixtures were assayed for hydrazine, ammonium ion and Tc^{IV} and Tc^{V} content. The results obtained for the oxidation profile of hydrazine over time with varying acidity are presented in Figure 2.12.

For comparison the rate of hydrazine destruction at the lower nitrate ion concentration of 0.65 mol dm^{-3} as a function of HBF_4 concentration is also presented with the hydrazine destruction profile for the 2.0 mol dm^{-3} nitrate system in Figure 2.13.

It is clearly evident from this figure that there is a dramatic decrease in the rate of the fast reaction stage between 1.0 and 2.0 mol dm^{-3} HBF_4. This sudden change in the reaction rate is most likely to be due to the presence of the nitrate ion in a large excess over acid at 1.0 mol dm^{-3} HBF_4 and in equal concentrations at 2.0 mol dm^{-3}. Thus the rate of the fast reaction seems to be severely limited when the nitrate ion and acid concentrations approach parity.

The lower of the two lines on figure 2.13, i.e., that for 0.65 mol dm^{-3} nitrate ion concentration, displays no such discontinuity with increasing acidity, presumably because acid is in excess over nitrate ion over the entire range. It can also be seen that there is fair agreement in the rate of increase in the 'fast reaction' rate with increasing acidity for both nitrate concentrations employed, once the acid is in excess over nitrate ion.

The yields of ammonium ions are presented in Table 2.2; as with the 0.65 mol dm^{-3} nitrate system, the yield of ammonium ions falls with increasing acidity. Increasing the nitrate ion concentration to 2.0 mol dm^{-3} does, however, seem to inhibit the production of ammonium nitrate; the yields are reduced by about 10% at each acidity studied.

Figure 2.12 : The Oxidation of Hydrazine over Time with Increasing Tetrafluoroboric Acid Concentration

[Tc]	:	1.6×10^{-3} M
$[N_2H_5^+H_2O]$	:	0.1 M
$[NaNO_3]$	:	2.0 M
$[HNO_3]$	:	0.05 M
$[BF_4^-]_{Total}$	:	3.6 M
Temp.	:	35°C

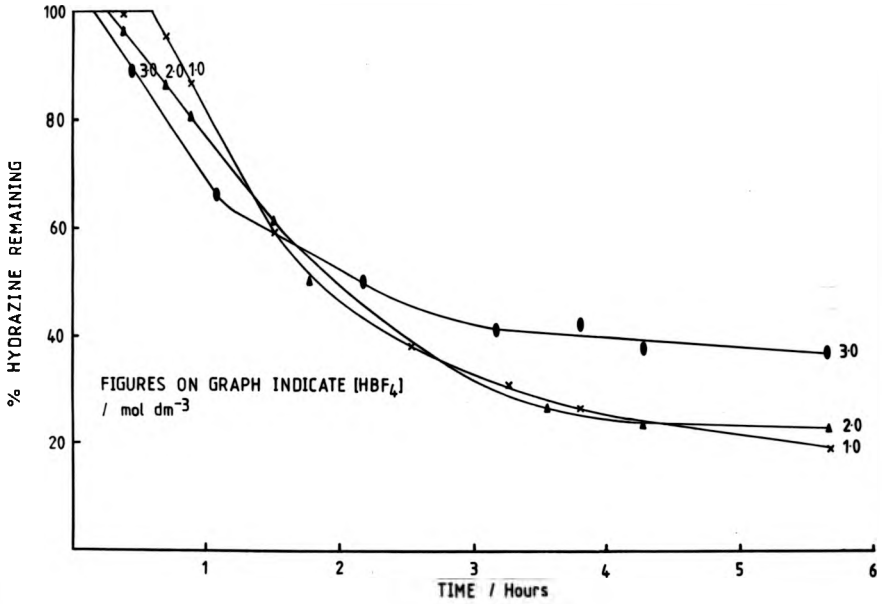

100
80
60
40
20
% HYDRAZINE REMAINING
3·0 2·0 1·0
FIGURES ON GRAPH INDICATE [HBF4]
/ mol dm-3
3·0
2·0
1·0
1
2
3
4
5
6
TIME / Hours

Figure 2.13 : Variation in the Rate of Hydrazine Oxidation with Tetrafluoroboric Acid Concentration for 0.6 and 2.0 M $NaNO_3$

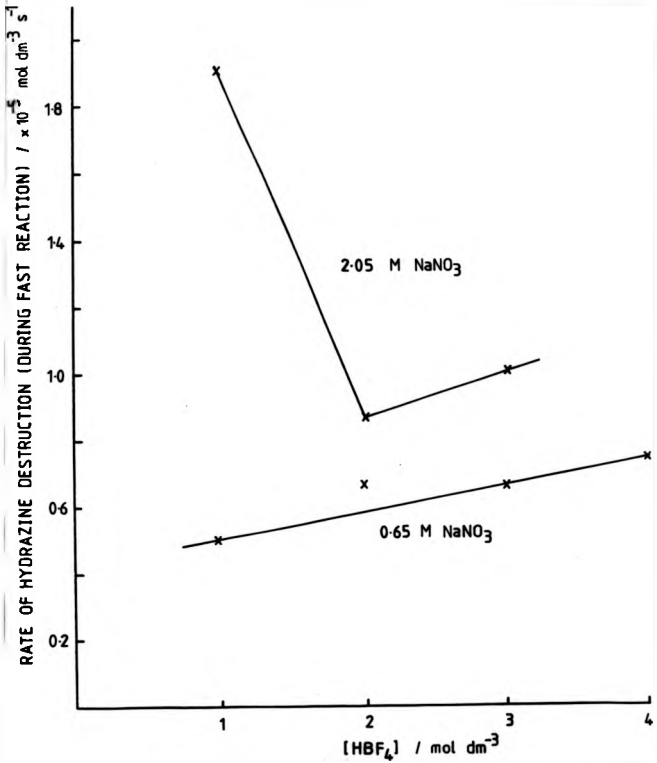

RATE OF HYDRAZINE DESTRUCTION (DURING FAST REACTION) / x 10^-5 mol dm^-3 s^-1
1·8
1·4
1·0
0·6
0·2
2·05 M NaNO3
0·65 M NaNO3
1
2
3
4
[HBF4] / mol dm^-3

Table 2.2 : Variation in the Yield of Ammonium Ions with Increasing Tetrafluoroboric Acid Concentration

$[HBF_4]$ /mol dm^{-3}	1	2	3
$[NH_4^+]$ produced /mol dm^{-3}	0.0221	0.0214	0.0139
$[N_2H_4]$ Oxidised /mol dm^{-3}	0.0806	0.0766	0.0626
Yield of NH_4^+ / mole % based on hydrazine loss	27.4	27.9	22.2

2.3 The Effect of Nitrate Ion on the Tc-Hydrazine Reaction

(Using Sodium Tetrafluoroborate to Maintain Ionic Strength)

In order to investigate the specific role of nitrate ion in the reaction, a study was carried out in which the nitrate ion concentration was varied, with the ionic strength being maintained using sodium perchlorate. In these experiments it was not known (and certainly unexpected) that the normally inert perchlorate ion could function as an oxidant in this system. This however turned out to be the case and hence the kinetics observed were due to simultaneous alteration of the nitrate and perchlorate ion concentrations. This system is dealt with in section 3.1.

Due to this interference by the perchlorate ion, the tetrafluoroborate anion was adopted to maintain constant ionic strength, as it was anticipated that it would be genuinely inert. The results of this study show that increasing the nitrate ion concentration increases the rate of the fast reaction and slightly decreases the initiation period. The increase in the rate of oxidation of hydrazine during the fast reaction stage with increasing nitrate concentration is illustrated in Figure 2.14.

The rate of production of ammonium ions in the reaction shows a slight increase between 0.5 and 2.0 mol dm^{-3} nitrate ion concentration, after which doubling the nitrate ion concentration doubles the rate of reaction, as shown in Figure 2.15. However, the overall yield of ammonium ions falls with increasing nitrate ion concentration as shown in Table 2.3.

Figure 2.14 : Variation in the Rate of Hydrazine Oxidation during the Fast Reaction Stage with increasing Nitrate Ion Concentration at Constant Ionic Strength

[Tc]	:	1.6×10^{-3} M
$[N_2H_4]$	:	0.1 M
$[HNO_3]$	:	0.55 M
$[NaNO_3]$	:	Varied
$[NaBF_4]$	:	Varied
μ	:	6.05 M
Temp.	:	35^oC

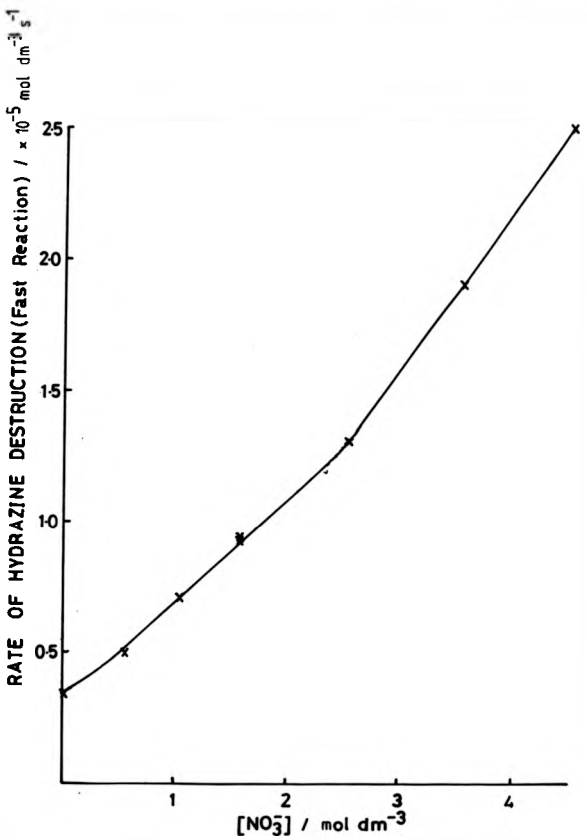

RATE OF HYDRAZINE DESTRUCTION (Fast Reaction) / × 10⁻⁵ mol dm⁻³ s⁻¹
25
20
15
10
0·5
1
2
3
4
[NO3⁻] / mol dm⁻³

Figure 2.15 : Rate of Production of Ammonium Ions with Increasing Nitrate Ion Concentration

[Tc]	:	1.6×10^{-3} M
$[N_2H_4]$	:	0.1 M
$[HNO_3]$	:	0.55 M
$[NaNO_3]$	:	Varied
$[NaBF_4]$	:	Varied
μ	:	6.05 M
Temp.	:	35°C

RATE OF AMMONIUM ION PRODUCTION (Fast Reaction) / ×10⁻⁶ mol dm⁻³ s⁻¹
6
5
4
3
2
1
2
3
4
[NO3⁻] / mol dm⁻³

Table 2.3 : Variation in the Yield of Ammonium Ions with increasing Nitrate Ion Concentration at Constant Ionic Strength

$[NO_3^-]$ /mol dm^{-3}	0.55	1.05	1.55	2.55	3.55	4.55
$[NH_4^+]$ Produced /mol dm^{-3}	0.0265	0.0280	0.0238 0.0220	0.0238	0.0201	0.0190
$[N_2H_4]$ oxidised /mol dm^{-3}	0.0693	0.0733	0.0774 0.0646	0.0605	0.0626	0.0666
Yield NH_4^+ / mol % based on hydrazine loss	38.3	38.2	30.7 34.1	39.3	32.1	28.5

2.4 Computer Simulation of the Tc-Hydrazine Reaction in a Nitric Acid-Sodium Nitrate System

The reaction has been computer simulated using software written specifically for the purpose by P. D. Wilson (15). In a paper by Garraway and Wilson (27) they obtained an excellent fit to hydrazine oxidation with a poorer, but still acceptable fit for Tc^{IV} and Tc^{V}. A set of 'best fit' rate constants were proposed which applied only to a system containing 1.6×10^{-3} mol dm^{-3} TcO_4^-, 0.1 mol dm^{-3} N_2H_4 and 1.2 mol dm^{-3} HNO_3.

One object of our work was to extend the scope of the Garraway and Wilson simulation, which was confined to single, or narrow ranges of reactant concentrations, to enable a range of reactant concentrations to be covered and, if necessary, to modify their proposed reaction scheme.

The only major modification that proved to be necessary was to introduce the acid-dependent oxidation of Tc^{VI} to Tc^{VII} by nitrate ion to account for the observed inhibition of the reaction with increasing concentrations of nitric acid. However, it transpired that the acid-dependence of the termination reaction varied in a non-linear way and it therefore proved necessary to introduce a new variable K(12), the value of which depends on acidity, in order to achieve a close fit to the experimental data.

Similarly the value of the rate constant for the initiation reaction needed slight adjustment to enable variations in the overall reaction profile due to changes in the initial concentration of hydrazine to be studied. The reaction scheme and the individual rate constants used in our simulations are as follows:

		Rate Constants /mol dm^{-3} s^{-1}
1) $Tc(VII) + N_2H_4$	→ $Tc(VI) + N_2H_{4(ox)}$	$K(1)$ 2.22 x 10^{-3}
2) $Tc(VI) + N_2H_4$	→ $Tc(IV) + N_2H_{4(ox)}$	$K(2)$ 0.236
3) $Tc(IV) + Tc(VII)$	→ $Tc(VI) + Tc(V)$	$K(3)$ 3.056
4) $Tc(IV) + NO_3^-$	→ $Tc(VI) + NO_2^-$	$K(4)$ 1.25 x 10^{-3}
5) $Tc(V) + N_2H_4$	→ $Tc(IV) + N_2H_{4(ox)}$	$K(5)$ 0.25
6) $Tc(VI)+NO_3^-+2H^+$	→ $Tc(VII) + NO_2^- + H_2O$	$K(6)[5x10^{-4}+K(12)^a]$
7) $Tc(V) + NO_3^-$	→ $Tc(VII) + NO_2^-$	$K(7)$ 1.389 x 10^{-3}
8) $NO_2^- + N_2H_4$	→ $HN_3 + 2H_2O$	$K(8)$ 0.1389
9) $HN_3 + NO_2^- + H^+$	→ $N_2 + NH_4^+ + NO_2$	$K(9)$ 1.389 x 10^{-2}

[a] - K(12) is acid dependent (see text)

Here $N_2H_{4(ox)}$ represents some oxidation product of N_2H_4, for instance N_2H_3. The equations employed provide a basic scheme which allows a passable representation of the experimental results to be obtained. It has proved necessary to alter the value of some of the rate constants with changing reactant concentration. It is therefore accepted that the rate constants accompanying the equations are not absolute values, but merely "best-fit" values, which provide an adequate fit to the observed data. Further work is required in order to establish the mutual effects each reaction in the scheme has on others.

2.4.1 Simulation of the Effects of Nitric Acid

As already mentioned the effect of nitric acid on the observed kinetics of the reaction is complex. It was found possible to simulate the residual hydrazine concentration and the correct rate of hydrazine loss during the fast reaction stage, but not,

simultaneously, the correct initiation period at low acidities, although fair agreement between the computed and experimental initiation periods was achieved at $[H_3O^+] \geq 3.0$ mol dm^{-3}. Figure 2.16 provides a comparison between the experimental results and those simulated.

The introduction into the equation simulating the termination reaction of the variable K(12), which can be assigned a value depending on acid concentration, allowed the correct 'plateau' concentration of hydrazine to be simulated. Interpolation from Figure 2.17 enables one to obtain the value of K(12) required for any acid concentration between 0.1 and 5.0 mol dm^{-3}, assuming the nitrate concentration remains constant.

2.4.2 Simulation of the Effects of Varying the Initial Concentration of Hydrazine

The experimental results we have simulated were obtained from Garraway and Wilson (27). In their study of the dependence of the rate of the Tc-hydrazine reaction on the initial hydrazine concentration, they employed a single nitric acid concentration, namely 1.2 mol dm^{-3}, without adding sodium nitrate to increase the nitrate concentration. The reason for this was that the acid concentration expected in the IBX column in the THORP process is about 1.2 mol dm^{-3}.

In order to simulate the results from this system with a low total concentration of nitrate ion, i.e. 1.2 as compared to 7.0 mol dm^{-3}, it was found necessary to adopt rate constants having values close to those published by Garraway and Wilson (15) which were intended for use at this acidity, but at the lower hydrazine concentration of 0.1 mol dm^{-3}

The rate constants used are given in Table 2.5. Using these

Figure 2.16 : Computer Simulation of the Effects of Varying Nitric Acid Concentration on the Kinetics of the TcO_4^--Hydrazine Reaction

$[TcO_4^-]$	:	1.6×10^{-3} mol dm^{-3}
$[HNO_3]$	:	Varied
$[N_2H_5NO_3]$	:	0.1 mol dm^{-3}
$[NO_3^-]_{Total}$	:	7.0 mol dm^{-3}
Temp.	:	35°C

Table 2.4 : Variation in the Value of K(12) with $[HNO_3]$

$[HNO_3]$ /mol dm^{-3}	5	4	3	2	1	0.5	0.1
K(12) / 10^{-4} mol dm^{-3} s^{-1}	1.11	1.32	1.43	1.75	2.92	3.12	30.1

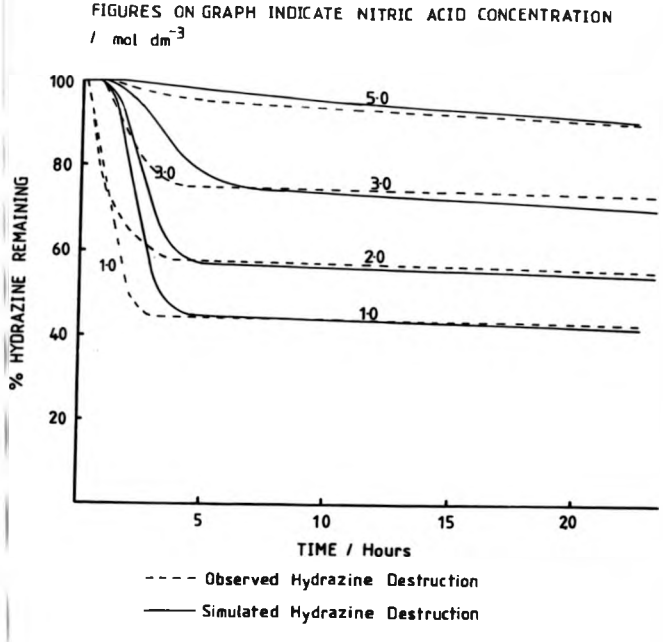
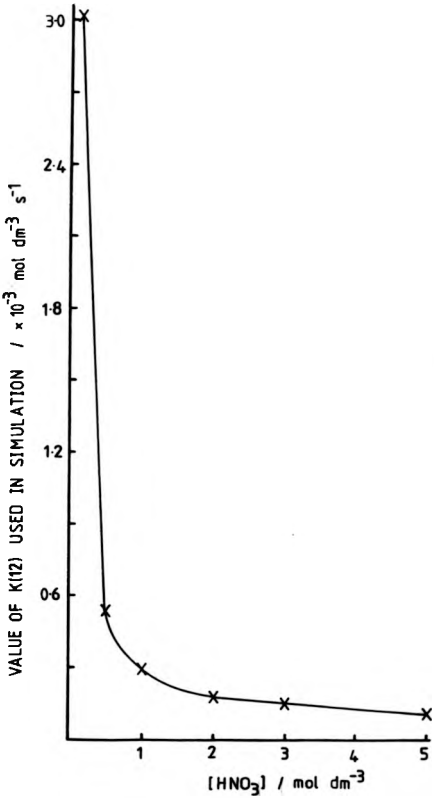

FIGURES ON GRAPH INDICATE NITRIC ACID CONCENTRATION
/ mol dm⁻³
% HYDRAZINE REMAINING
100
80
60
40
20
5·0
3·0
3·0
2·0
1·0
1·0
5
10
15
20
TIME / Hours
Observed Hydrazine Destruction
Simulated Hydrazine Destruction

Table 2.5 : Values of "Best-Fit" Rate Constants used to simulate Variations in the Initial Hydrazine Concentration

Constant	Rate / mol dm^{-3} s^{-1}
K(1)	1×10^{-5}
K(2)	0.208
K(3)	2.5
K(4)	8.33×10^{-3}
K(5)	0.208
K(6)	5.56×10^{-4}
K(7)	2.78×10^{-3}
K(8)	0.139
K(9)	1.39×10^{-2}
K(12)	Varied

Figure 2.17 : Plot of Value of K(12) Required for Simulation of Hydrazine Oxidation Versus Nitric Acid Concentration


3·0
2·4
1·8
1·2
0·6
VALUE OF K(12) USED IN SIMULATION / × 10⁻³ mol dm⁻³ s⁻¹
1
2
3
4
5
[HNO3] / mol dm⁻³

constants and the equation set already given, Figure 2.18 was obtained. It can be seen that only the simulated plot of hydrazine destruction for a system which initially contained 0.1 mol dm^{-3} N_2H_4 is acceptable.

For the other plots the rates of hydrazine loss during the fast reaction stage are acceptable, but the initiation period is not. By adjusting K(1) in a manner similar to K(12) for the nitric acid simulation, it was found possible to obtain the correct induction period prior to commencement of the fast reaction stage. Whilst the major effect of altering K(1) manifests itself in changes in the initiation period, small changes also occur in the rate of hydrazine loss during the fast reaction stage. Figure 2.19 demonstrates the much better agreement between the new simulated data and the experimental results. Marked deviation is confined to the results at 0.2 mol dm^{-3} hydrazine, which may simply reflect some error in the Garraway-Wilson results.

2.4.3. Simulation of the Effects of Technetium Concentration on the Hydrazine Oxidation Profile

As in Section 2.4.2., the experimental results showing the effects on the reaction profile of variations in the technetium concentration were those of Garraway and Wilson (27). The reaction conditions employed are listed on the title page of Figure 2.20. The rate constants used are the same as those for the hydrazine simulation (with the value for K(1) set at the value for $[N_2H_4]$ = 0.1 mol dm^{-3}). A slight variation in the value of K(12), depending on the technetium concentration, enables a good agreement with the experimental results to be obtained. The simulated and observed results are presented in Figure 2.20 and the appropriate values of K(12) are given in Table 2.8. (given on the title page of Fig.

Figure 2.18 : Incorrect Computer Simulation of the Effects of Varying Initial Hydrazine Concentration on the Kinetics of the Tc-Hydrazine Reaction in Nitric Acid (obtained by Varying only K(12) with Hydrazine Concentration)

(Experimental Results obtained from J Garraway and P D Wilson (27))

[Tc]	:	1.6×10^{-3} mol dm^{-3}
$[HNO_3]$	:	1.2 mol dm^{-3}
$[N_2H_5NO_3]$	:	Varied
$[NO_3^-]_{total}$	:	Varied
Temp.	:	35^oC

Table 2.6 : Variation in the Values of K(12) used with Initial Hydrazine Concentration

$[N_2H_5NO_3]$ / mol dm^{-3} s^{-1}	0.244	0.203	0.145	0.094	0.050
K(12) / 10^{-4} mol dm^{-3} s^{-1}	2.19	2.22	2.28	2.36	2.47

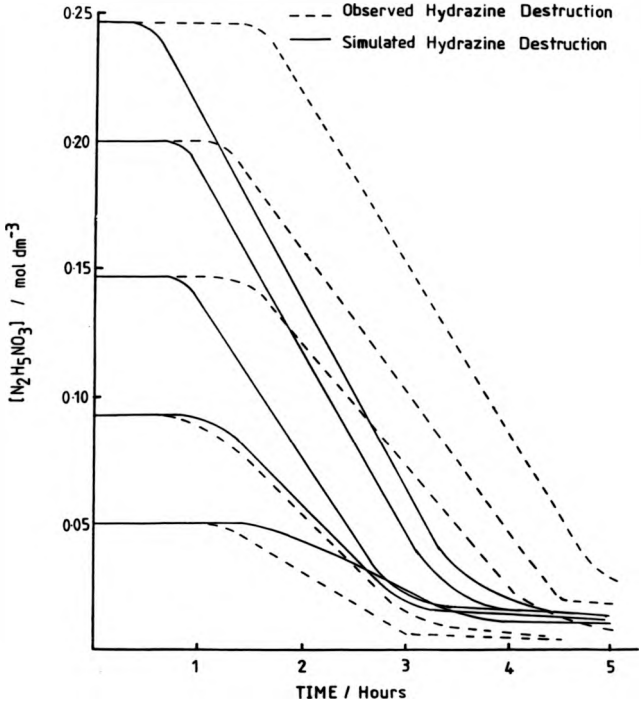

Observed Hydrazine Destruction
Simulated Hydrazine Destruction
0·25
0·20
0·15
0·10
0·05
[N2H5NO3] / mol dm-3
1
2
3
4
5
TIME / Hours

Figure 2.19 : Computer Simulation of the Effects of Varying Initial Hydrazine Concentration on the Kinetics of the Tc-Hydrazine Reaction in Nitric Acid.

(Experimental Results obtained from J. Garraway and P D Wilson (27))

[Tc]	:	1.6×10^{-3} mol dm^{-3}
$[HNO_3]$	:	1.2 mol dm^{-3}
$[N_2H_5NO_3]$	:	Varied
$[NO_3^-]_{Total}$	:	Varied
Temp.	:	35°C

Table 2.7 : Variation in the Values of K(1) and K(12) with Initial $[N_2H_5NO_3]$

$[N_2H_5NO_3]$ /mol dm^{-3}	K(1) /mol dm^{-3} s^{-1}	K(12) /mol dm^{-3} s^{-1}
0.244	1.11×10^{-10}	2.19×10^{-4}
0.203	1.36×10^{-8}	2.22×10^{-4}
0.145	1.94×10^{-8}	2.28×10^{-4}
0.094	5.56×10^{-6}	2.36×10^{-4}
0.050	1.11×10^{-4}	2.47×10^{-4}

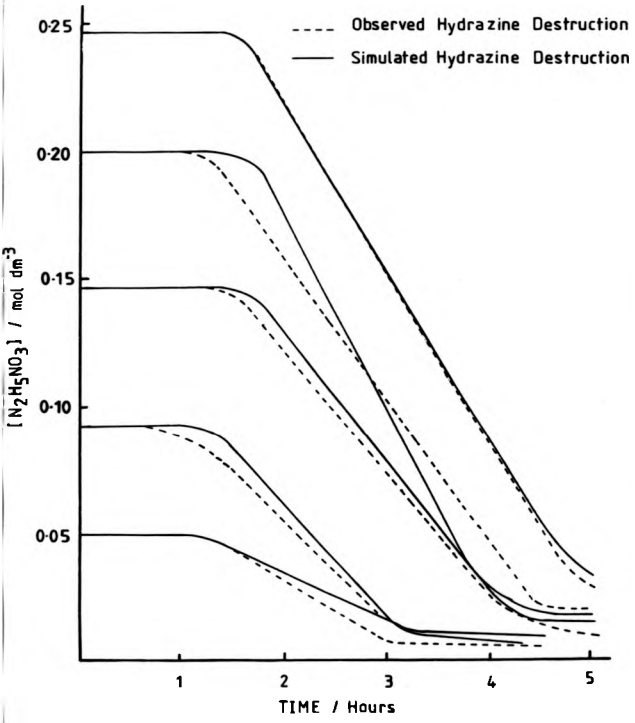

Observed Hydrazine Destruction
Simulated Hydrazine Destruction
0·25
0·20
0·15
0·10
0·05
[N2H5NO3] / mol dm-3
1
2
3
4
5
TIME / Hours

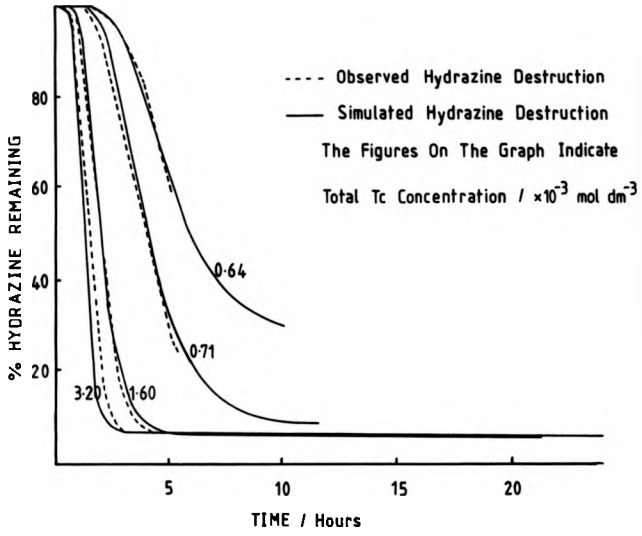
Figure 2.20 : Computer Simulation of the Effects of Varying the Initial Tc Concentration on the Kinetics of the Tc-Hydrazine Reaction in Nitric Acid

(Experimental Results obtained from J. Garraway and P D Wilson (27))

[Tc]	:	Varied
$[HNO_3]$	:	1.2 mol dm^{-3}
$[N_2H_5NO_3]$	:	0.1 mol dm^{-3}
$[NO_3^-]_{Total}$	:	1.3 mol dm^{-3}
Temp.	:	35°C

Table 2.8 : Variation in the Value of K(12) with [Tc]

[Tc] / 10^{-3} mol dm^{-3}	3.2	1.6	0.71	0.64
K(12) / 10^{-4} mol dm^{-3} s^{-1}	3.75	1.94	1.11	2.36


---- Observed Hydrazine Destruction
—— Simulated Hydrazine Destruction
The Figures On The Graph Indicate
Total Tc Concentration / ×10⁻³ mol dm⁻³
% HYDRAZINE REMAINING
80
60
40
20
0·64
0·71
3·20
1·60
5
10
15
20
TIME / Hours

2.20). The value of K(12) depends somewhat on Tc concentration.

2.4.4 Simulation of the Effects of Adding Uranium or Plutonium on the Kinetics of the Tc-Hydrazine Reaction

The complex reaction that occurs between TcO_4^- and hydrazine in a nitric acid medium is only the basic system as far as nuclear fuel reprocessing is concerned. A more realistic study would involve the further complicating addition of uranium(IV) and/or plutonium(III) or (IV) to the reaction mixtures.

The reactions and kinetics of such a multi-component system have already been studied in some detail by Garraway and Wilson (27) and several Russian groups, (9, 25, 38, 104). As with the reaction schemes formulated for the basic Tc-hydrazine reaction, there is some controversy about the exact pathways followed when uranium and plutonium are present. A full list of published reactions that have been proposed is presented in the introduction (Tables 1.2 - 1.4).

We have reproduced with reasonable success the kinetics of hydrazine loss from solutions containing plutonium(IV), using the equation set and rate constants presented in Table 2.9, as illustrated in Fig. 2.21. The apparent divergence between the simulated results of hydrazine oxidation and those obtained by Garraway and Wilson is due to no experimental data points being collected by Garraway for the first 12 hours of the reaction. Thus, the initial level stage of the hydrazine oxidation profile was obtained by extrapolation from the initial reaction conditions. The production profile of Pu^{III} does not exhibit such a good fit, although it does follow the general trend.

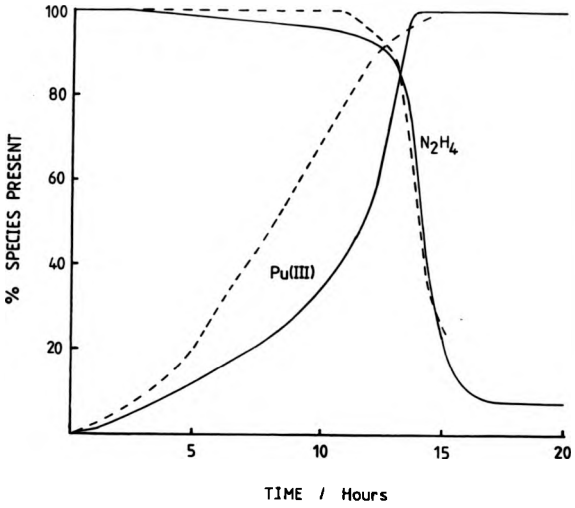
Table 2.9 : Reactions and Rate Constants used in the Simulation of the Effects of Adding Plutonium(IV) to a Tc-N_2H_4-HNO_3 Solution

				Rate / mol dm^{-3} s^{-1}
1	Tc(VII) + N_2H_4	→	Tc(VI) + N_2H_4 ox	1×10^{-5}
2	Tc(V) + N_2H_4	→	Tc(IV) + N_2H_4 ox	0.208
3	Tc(IV) + Tc(VII)	→	Tc(V) + Tc(VI)	2.5
4	Tc(IV) + NO_3^-	→	Tc(VI) + NO_2^-	8.33×10^{-3}
5	Tc(VI) + N_2H_4	→	Tc(IV) + N_2H_4 ox	0.208
6	Tc(VI) + NO_3^-	→	Tc(VII) + NO_2^-	5.56×10^{-4}
7	Tc(V) + NO_3^-	→	Tc(VII) + NO_2^-	2.78×10^{-3}
8	NO_2^- + N_2H_4	→	NH_3 + $2H_2O$	0.139
9	Tc(IV) + Pu(IV)	→	Tc(V) + Pu(III)	3.89
10	Tc(V) + Pu(IV)	→	Tc(VI) + Pu(III)	3.89
11	Tc(VI) + Pu(IV)	→	Tc(VII) + Pu(III)	5.56×10^{-2}
12	Tc(IV) + NO_2^-	→	Tc(VI) + NO	2.778
13	Pu(IV) + NO_2^-	→	Pu(III) + NO	2.87×10^{-3}

Here (ox) represents some unspecified oxidation product of hydrazine, e.g. N_2H_3 or N_2H_2

Figure 2.21 : Computer Simulation of the Effects of Adding Plutonium as Pu(IV) on the Kinetics of Hydrazine Oxidation and Pu(III) Production (Experimental Results obtained from J. Garraway and P D Wilson (27))

[Tc]	:	1.6×10^{-3} M
$[N_2H_5NO_3]$	:	0.1 M
$[HNO_3]$	:	1.2 M
$[NO_3^-]_{Total}$	:	1.3 M
[Pu(IV)]	:	0.00123 M
Temp.	:	35^oC


100
80
60
40
20
% SPECIES PRESENT
N_2H_4
Pu(III)
5
10
15
20
TIME / Hours
Observed Results
Simulated Results

2.5 Discussion

A key feature of the kinetic profiles for the hydrazine destruction reaction is that, following the fast stage, the reaction invariably ceases, giving rise to a 'plateau' or 'residual' concentration of N_2H_4. This point is reached when the initiation reaction, equation 2.10, of rate R_1 which supplies the Tc^{VI} necessary for other reactions in the scheme, is outstripped by the rate, R_2 of the termination reaction which removes Tc^{VI}, equation 2.11.

$$TcO_4^- + N_2H_4 \xrightarrow{R_1} Tc^{VI} + N_2H_3 + H^+ \qquad [2.10]$$

$$2Tc^{VI} + NO_3^- + 2H^+ \xrightarrow{R_2} 2TcO_4^- + NO_2^- + H_2O \qquad [2.11]$$

When $R_1 > R_2$, the oxidation of hydrazine proceeds rapidly and the system is able to enter the fast reaction stage due to the production of large amounts of Tc^{VI}. When R_1 is equal to R_2, the rate of formation of Tc^{VI} is equal to its rate of reoxidation back to TcO_4^-, and hence the reaction does not enter the fast reaction stage, but rather a slow decline in hydrazine concentration is observed as is the case for 5.9 mol dm^{-3} acid, Figure 2.6. This competition between the initiation and termination reactions is a key feature of the computer simulation, where it was found necessary to adjust the efficiency of the termination reaction in order to achieve the desired results.

Finally when $R_1 < R_2$, the reaction enters its termination stage when the reduced states of technetium are all converted back to TcO_4^- via Tc^{VI}.

The dependence of the reaction rate profile on acid concentration can be partially explained by formulating the following two equations:

$$-\frac{d[TcO_4^-]}{dt} = R_1 = k_1[TcO_4^-][N_2H_4] \qquad \text{(initiation)} \quad [2.12]$$

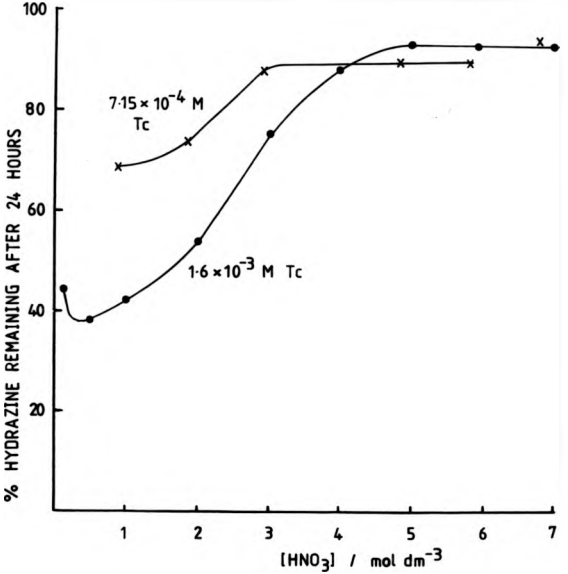
$$-\frac{d[TcO_4^{2-}]}{dt} = R_2 = k_2\,[TcO_4^{2-}][H^+]^2[NO_3^-] \quad \text{(termination)} \quad [2.13]$$

In this scheme the initiation reaction is independent of acidity whilst the termination reaction is dependent on the square of acid concentration. Thus as the acidity is raised, the termination reaction increases in importance until at 5 mol dm^{-3} acid (for a reaction mixture containing 1.6 x 10^{-3} mol dm^{-3} Tc), its rate R_2 is comparable to that of the initiation reaction R_1.

A way of illustrating the role of the fast reaction stage which is the reduction of Tc^{VI} to Tc^{IV} by hydrazine and hence of the effectiveness of the termination reaction is to plot the percentage of hydrazine remaining versus acidity, as in Figure 2.22. This shows the dependence of the percentage of hydrazine remining 24 hours after initiation at 7.2 x 10^{-4} and 1.6 x 10^{-3} mol dm^{-3} Tc concentrations upon increasing nitric acid concentration. It can be seen that both curves display a region where large amounts of hydrazine are destroyed in the reaction, the amount of hydrazine eventually destroyed decreasing with increasing acidity. At the lower Tc concentration (7.2 x 10^{-4} mol dm^{-3}), the hydrazine destruction levels out at about 3 mol dm^{-3} acidity, giving an approximately 10% loss of hydrazine at higher acidities.

For the system with [Tc] = 1.6 x 10^{-3} mol dm^{-3}, the acid inhibition of the fast reaction appears at 5 mol dm^{-3} acid. The inflection in the curve at acidities between 0.1 and 0.5 mol dm^{-3} is presumably due to the low acid concentration limiting the reaction rate. This can be explained by the finding of Garraway and Wilson (15) that the oxidation of 1 mole of hydrazine consumes 0.5 moles of protons, thus

Figure 2.22 : Percentage of Unreacted Hydrazine Remaining after 24 hours with Varying Nitric Acid Concentration


100
80
60
40
20
% HYDRAZINE REMAINING AFTER 24 HOURS
7·15 × 10⁻⁴ M Tc
1·6 × 10⁻³ M Tc
1
2
3
4
5
6
7
[HNO3] / mol dm⁻³

if the acidity of a reaction mixture is decreased sufficiently, then the low proton concentration will limit the reaction rate.

In order to understand more fully this complex behaviour, we must consider the role both of the nitrate ion and the protons in the reaction. Nitrate ion is involved in the re-oxidation steps of the reduced oxidation states of technetium, i.e., Tc^{IV}, Tc^{V} and Tc^{VI}. The equations below give possible reactions between these oxidation states and the nitrate ion, and are used in the computer simulation of the Tc-hydrazine reaction.

$$Tc^{IV} + NO_3^- \rightarrow Tc^{VI} + NO_2^- \qquad [2.14]$$

$$Tc^{V} + NO_3^- \rightarrow TcO_4^- + NO_2^- \qquad [2.15]$$

$$2Tc^{VI} + NO_3^- + 2H^+ \rightarrow 2TcO_4^- + NO_2^- + H_2O \qquad [2.16]$$

The chemical structure of these complexes is uncertain, although oxo-ions for instance TcO^{3+} (16) or hydrolysed species such as $TcO(OH)_2$ (2,15) have been proposed. It is thought that in the fast reaction cycle, where Tc^{IV} is oxidised by the nitrate ion, that a two-electron oxidation takes place to produce Tc^{VI}. If this is the case, the reaction should be independent of acid concentration. This reaction is the rate-determining step in the "fast reaction" stage, thus the overall rate of the fast reaction is limited by the rate at which Tc^{VI} can be regenerated from Tc^{IV}.

The rate of change of Tc^{IV} can be defined by the following equation:

$$\frac{d\,[Tc^{IV}]}{dt} = R_3 = k_3\,[Tc^{IV}]\,[NO_3^-] \qquad [2.17]$$

Whilst the fast reaction stage is unaffected by acid, the rate of the termination reaction (equation 2.16) which is dependent on the square of the acid concentration increases sharply with acidity. From Figure 2.7 it is evident that below 0.5 mol dm^{-3} acidity, a very high rate of hydrazine oxidation is observed. Between 0.5 and

0.1 mol dm^{-3} nitric acid a very large decrease in the reaction rate occurs; thereafter a steady and considerable decline in reaction rate is evident. It is possible to explain these observations in terms of the relative rates of the fast reaction (R_3) and termination reaction (R_2). For nitric acid concentrations less than 0.5 mol dm^{-3} the relative rate of the fast reaction is far greater than that of the termination stage, so a very rapid loss of hydrazine is expected. At acidities near to 1.0 mol dm^{-3} the relative rates of the two equations become comparable, resulting in a steep decline in the rate of the fast reaction. Thereafter the rate of the termination reaction increases sharply, producing the rapid decrese in the rate of hydrazine oxidation as the fast stage is starved of Tc^{VI}, until at 6.7 mol dm^{-3} acid the reaction virtually ceases.

These conjectures are supported by the computer simulation of the nitric acid system which shows the increasing prominence of the termination stage as the acidity increases.

The oxidising power of HNO_3 is mainly due to the presence of undissociated acid molecules. Thus the HNO_3 molecule can function both as an oxidant and a proton donor. As the concentration of nitric acid is raised, the amount of undissociated acid will increase, and with it, the oxidising power of the solution.

Tetrafluoroboric acid is a stronger acid than nitric acid, and consequently in a solution containing both of these acids, a greater proportion of the tetrafluoroboric acid will dissociate at the expense of the dissociation of HNO_3, with the result that the concentration of HNO_3 molecules will be increased at a given stoichiometric total acid concentration. Similarly in a solution containing HBF_4 and a nitrate salt, the HBF_4 will dissociate almost

completely, inducing the partial protonation of the nitrate ions, to give rise to a more powerfully oxidising solution.

There are two possible explanations for the unexpected acidity dependence observed for the rate of the Tc-hydrazine reaction in solutions containing HBF_4 and $NaNO_3$. This may be attributed either to an enhanced reactivity of the Tc^{VI} species on protonation or to the direct oxidation of hydrazine or its degradation products, by the undissociated nitric acid.

It is widely accepted that the technetate(VI) ion is a transient species in aqueous solution. A pulse radiolysis study by Libson et al. (33) showed that in alkaline solution the technetate ion does not decay over the time-resolution of the equipment (several milliseconds), but in acid solution it decays at a measurable rate (i.e. over several ms).

It is possible that nitric acid protonates the TcO_4^{2-} ion, giving either the singly - or doubly protonated species. In this form, the Tc^{VI} may be both less transient and less susceptible to oxidation by nitrate ions, but be even more capable of functioning as an oxidant. Thus the rate of the termination step in the Tc-hydrazine reaction, in which Tc^{VI} is oxidised to TcO_4^- by nitrate ion, could be reduced while leaving the kinetics of the fast reaction stage unaffected or even enhanced, in which case the net rate of oxidation of hydrazine would remain high.

The alternative explanation involves the direct oxidation of hydrazine by HNO_3. We have found that all the hydrazine in a solution is oxidised in under 24 hours by concentrated nitric acid (16 mol dm^{-3}), this oxidation presumably takes place due to the presence of large amounts of the undissociated acid. Decreasing the acid concentration from 16 to 8 mol dm^{-3} effectively prevents this

oxidation by nitric acid. During the course of the Tc-hydrazine reaction it is thought that several intermediate oxidation products of hydrazine will be present, (albeit as transients in some cases), for instance, N_2H_2, N_2H_3 and N_4H_4, the last of which dissociates to give nitrogen and hydrazine. The stability of N_2H_2 towards nitric acid in solution is unknown, but it may well be directly oxidised by HNO_3 rather than by technetium. Thus in the HBF_4-$NaNO_3$ systems the apparent increase in the rate of hydrazine oxidation could be due to the removal of partially oxidised species by undissociated nitric acid molecules rather than to an increase in the rate of their oxidation by technetium.

Of these two explanations the former is more probable as only a small increase in the rate of hydrazine oxidation was observed in systems based on HBF_4 media. The main difference between the results obtained from the HNO_3 and HBF_4-$NaNO_3$ media is the shortening of the initiation period with increasing acidity in the latter system, i.e. the opposite of the situation obtaining in nitric acid. As the length of the initiation period is governed by the build up of Tc^{VI} and its subsequent reduction to Tc^{IV}, we propose that a mechanism that results in a more efficient production of a Tc^{VI} species which is less susceptible to oxidation by nitrate would provide an adequate explanation for the observed results.

Further evidence for the decreased effectiveness of the termination reaction in HBF_4-$NaNO_3$ media comes from the analysis of the time-dependence of the concentrations of Tc^{IV} and Tc^{V} present during reaction. These results typically feature a broad peak in either the concentration profile of Tc^{IV} or Tc^{V} followed by a residual 'plateau' concentration of about 15% Tc^{IV} and 1% Tc^{V}.

Clearly if the termination reaction was maximally effective, then

any Tc^{VI} produced by the oxidation of Tc^{IV} or Tc^{V} would be rapidly converted to pertechnetate. However, the presence of a steady-state concentration of reduced technetium, and a steady decline in the concentration of hydrazine, shows that whilst Tc^{IV} or Tc^{V} are being oxidised by nitrate ion, presumably to Tc^{VI}, the Tc^{VI} is being reduced by hydrazine before it can be oxidised by the nitrate ion.

2.6 Conclusions

The kinetics of the Tc-catalysed oxidation of hydrazine by nitrate have been studied in the presence of both nitric and tetrafluoroboric acids.

In nitrate media the reaction typically displays an induction period during which no visible loss of hydrazine occurs, followed by a 'fast reaction stage' which consists of the very rapid oxidation of hydrazine by Tc^{VI}. This stage is accompanied by the copious evolution of nitrogen and the production of much Tc^{IV}. At the end of the fast reaction stage all the technetium is reoxidised to TcO_4^-; this conversion back to TcO_4^- always occurs before complete loss of hydrazine from the solution and consequently a 'plateau' concentration of hydrazine remains.

Increase in the concentration of nitric acid has several effects on the reaction kinetics, namely to increase the length of the initiation period, to decrease the rate of the fast reaction stage and to decrease the amount of pertechnetate reduced to species which can readily oxidise hydrazine.

The use of tetrafluoroboric acid in place of nitric acid, and with sodium nitrate as a source of nitrate ions, revealed some unexpected results. If acid is in excess over nitrate ion then a slight increase in the rate of the fast reaction with increasing acidity

occurs. However, the situation is reversed when nitrate ion is in excess over acid, as the acidity is raised and the concentrations of both ions approach parity, the rate of the fast reaction stage is reduced.

An investigation into the effects of nitrate ions on the reaction kinetics using tetrafluoroboric acid and with its sodium salt to maintain ionic strength shows that the nitrate ion has little effect on the rate of the initiation reaction, as expected. The major effect of nitrate is to increase the rates of hydrazine oxidation and ammonium ion production during the fast reaction stage. This effect is most likely achieved by means of a faster turn-over rate of Tc^{IV}.

The computer simulation program devised by Wilson (27) to enable modelling of the Tc-hydrazine reaction in nitric acid has been extended to incorporate simulation of the effects of altering the concentrations of nitric acid, hydrazine and technetium. Several new equations have also been introduced into the reaction scheme to enable modelling of the effects on loss of hydrazine of adding plutonium as Pu^{III} or Pu^{IV}.

3.1 The Effects of Replacing the Nitrate Ion with Perchlorate Whilst Maintaining Ionic Strength on the Kinetics of the Tc-Hydrazine Reaction

The initial investigation we conducted into the effects of the nitrate ion on the kinetics of the Tc-hydrazine reaction was carried out using perchloric acid instead of nitric acid, and with sodium perchlorate to maintain the ionic strength.

As already mentioned in Section 2.3, which deals with the role of nitrate in the Tc-N_2H_4 reaction in the presence of the inert BF_4^- ion, the perchlorate ion was found unexpectedly to function as an effective oxidant in the Tc-hydrazine reaction. Thus this section (Section 3.1) deals with reactions occurring in a system containing varying proportions of two anionic oxidants; the nitrate and perchlorate ions.

The effect of increasing the concentration of nitrate ions on the rate of hydrazine oxidation during the fast stage of reaction is illustrated in Figure 3.1. The production of ammonium ions was also followed, and the rate of their evolution during the fast reaction stage is presented in Figure 3.2. Both figures display extended linear dependences of the rates with increasing nitrate ion concentration. The rates of oxidation of hydrazine and of production of ammonium ions are governed by the following two equations, the constants being derived from the slopes of Figures 3.1 and 3.2 respectively :

$$-d[N_2H_4]/dt = 2.75 \times 10^{-6} [NO_3^-] \text{ mol dm}^{-3} \text{ s}^{-1}$$

$$d[NH_4^+]/dt = 4.85 \times 10^{-7} [NH_4^+] \text{ mol dm}^{-3} \text{ s}^{-1}$$

It can be seen that at low nitrate ion concentrations the

Figure 3.1 Dependence of the Rate of Hydrazine Oxidation during the Fast Stage of Reaction on Nitrate Ion Concentration

[Tc]	:	1.6×10^{-3} mol dm^{-3}
$[N_2H_5NO_3]$	:	0.1 mol dm^{-3}
$[HClO_4]$	:	0.5 mol dm^{-3}
$[NaNO_3]$	:	Varied
$[NaClO_4]$	:	Varied
μ	:	7.5 mol dm^{-3}
Temp.	:	$35^{o}C$

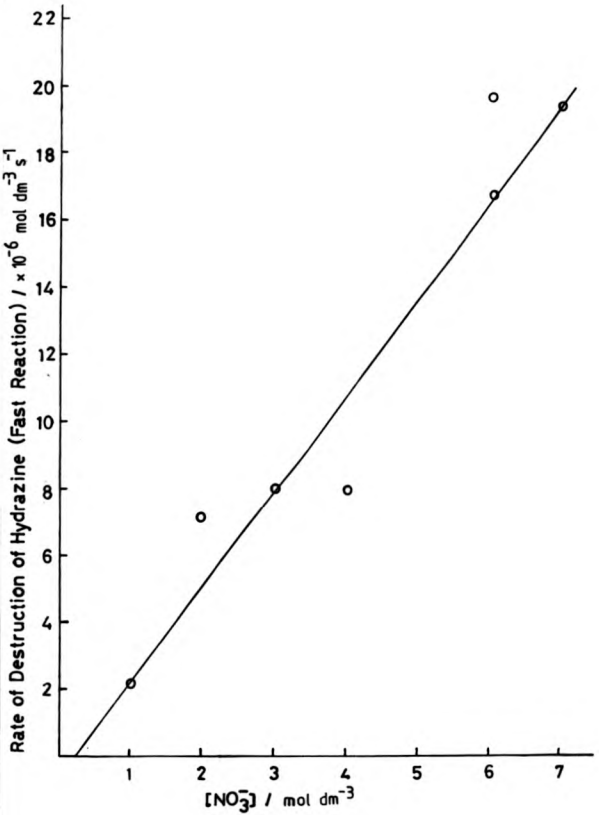

Rate of Destruction of Hydrazine (Fast Reaction) / $\times 10^{-6}$ mol dm^{-3} s^{-1}
22
20
18
16
14
12
10
8
6
4
2
1
2
3
4
5
6
7
[NO_3^-] / mol dm^{-3}

Figure 3.2 : Dependence of the Rate of Production of Ammonium Ions during the Fast Stage of Reaction on Nitrate Ion Concentration

[Tc]	:	1.6×10^{-3} mol dm^{-3}
$[N_2H_5NO_3]$	:	0.1 mol dm^{-3}
$[HClO_4]$	:	0.5 mol dm^{-3}
$[NaNO_3]$	:	Varied
$[NaClO_4]$	:	Varied
μ	:	7.5 mol dm^{-3}
Temp.	:	35°C

Rate of Ammonium Ion Production (Fast Reaction) / $\times 10^{6}$ mol dm^{-3} s^{-1}
4
3
2
1
1
2
3
4
5
6
7
[NO_3^-] / mol dm^{-3}

Tc-hydrazine reaction takes place relatively slowly. From this it can be inferred that at this low acidity (0.5 mol dm^{-3}, high concentrations of perchlorate ions (5.9 mol dm^{-3}) are ineffective in oxidising the reduced oxidation states of technetium. This inference is supported by the data obtained for the study of the perchloric acid dependence (Section 4.2).

As the concentration of nitrate is increased, the reaction rate increases proportionally. This increase in rate is due partly to the faster "turn-over" rate of the fast reaction cycle, in which Tc^{IV} is re-oxidised to Tc^{VI} by nitrate ion and partly to the increased production of nitrite ions which also react with hydrazine. Thus for each turn of the cycle one nitrate ion and two molecules of hydrazine are destroyed.

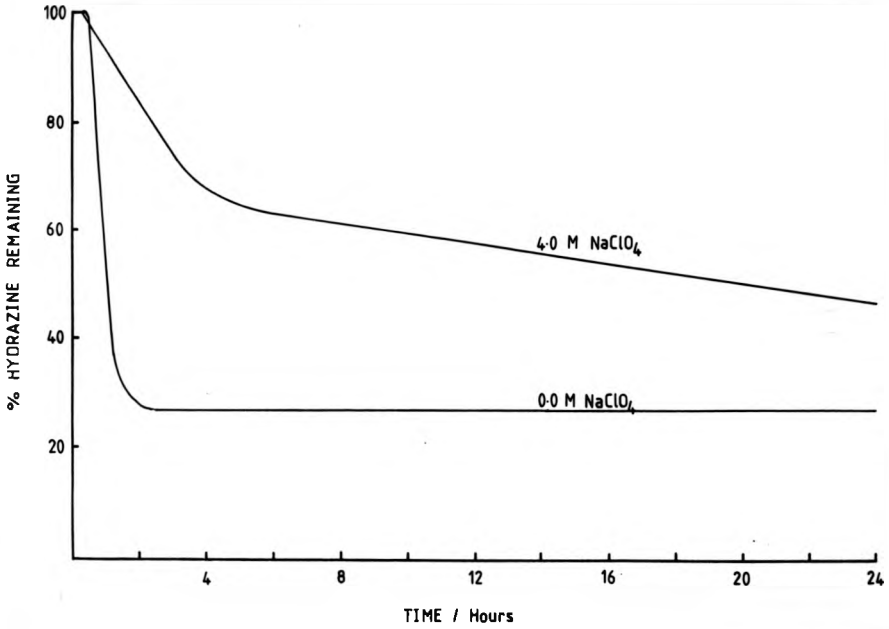
This view has some support from the results of Garraway and Wilson (15) who observed the loss of 0.05 moles of nitrate ion when oxidising 0.1 moles of hydrazine. Thus the observed increase in the rate of production of ammonium ions with increasing nitrate ion concentration will be due at least in part to the increasing prominence of the oxidation of hydrazine by nitrite ion.

It was considered possible that adding perchlorate ions to a nitrate-containing system inhibits the fast reaction stage. Two reaction mixtures were prepared, both containing perchloric acid (1.2 mol dm^{-3}) and sodium nitrate (2.8 mol dm^{-3}, but one containing, in addition sodium perchlorate (4.0 mol dm^{-3}). The variation in hydrazine concentration with time for both solutions is given in Figure 3.3.

The sodium perchlorate-free solution displays typical kinetics for a "nitrate system", i.e. an induction period, a fast reaction stage and a termination reaction which results in a steady state

Figure 3.3 : The Effects on the Rate of Hydrazine Oxidation of adding Sodium Perchlorate to an $HClO_4$-$NaNO_3$-TcO_4^- Solution

[Tc]	:	1.6×10^{-3} mol dm^{-3}
$[N_2H_5NO_3]$	:	0.1 mol dm^{-3}
$[NaNO_3]$	:	2.79 mol dm^{-3}
$[HClO_4]$	:	1.2 mol dm^{-3}
Temp.	:	35^oC


100
80
60
40
20
% HYDRAZINE REMAINING
4·0 M NaClO4
0·0 M NaClO4
4
8
12
16
20
24
TIME / Hours

concentration of residual hydrazine.

The other solution, however, showed markedly different kinetics, the only similarity being the length of the induction period. Clearly an alternative regime of chemical reactions must be in operation as the rate of the fast reaction has been reduced 7-fold and the termination reaction has been rendered ineffective, resulting in a continued slow oxidation of hydrazine extending beyond the 24-hour period of measurement (the "perchlorate-free" reaction is terminated after only 2 hours).

The cause of this change in the rate of hydrazine destruction probably originates in several factors. The perchlorate ion will compete with nitrate ion in oxidising any reduced Tc complexes present, leading ultimately to the production of oxychloro- or simple chloro-technetium complexes which may have different reactivities from the oxo species itself. It may also lead to an increased production of one oxidation state at the expense of another. Reaction mixtures having a high perchlorate concentration tend to display a steady-state level of Tc^{IV}, which persists for several weeks, which could reduce the amount of Tc available to react with hydrazine and therefore the rate of hydrazine oxidation. The addition of a large amount of a salt to a solution will also have a physical effect on the solution, i.e. it will tend to make it more structured as each added ion will be surrounded by its own "atmosphere" of solvating water molecules. This production of extensive ionic atmospheres around reagent ions and the reduction of the amount of free water in the solution will also play a significant role in determining the behaviour of the system. The effects of ionic strength will be dealt with in Section 3.2

3.2 The Effect on the Reaction Kinetics of Increasing the Ionic Strength Using Sodium Perchlorate

All reactions in solution are affected to some extent by changes in salt concentrations, which alter the activity coefficients of the ions present. The effects of electrolytes can be divided into two categories, known as the primary and secondary salt effects; the former refers to the influence of the electrolyte concentration on the activity coefficients whereas the latter is concerned with actual changes in the concentration of the reacting ions resulting from the addition of electrolytes, e.g. on the levels of dissociation of weak acids or bases.

In order to establish the effects of ionic strength on the kinetics of loss of hydrazine and production of ammonium ion during the course of the Tc-hydrazine reaction, a large number of reactions were carried out with ionic strengths varied from 0.9 to 6.6 mol dm^{-3} by adding sodium perchlorate. At ionic strengths of 4.0 mol dm^{-3} or less, the oxidation of hydrazine exhibits the 'normal' kinetic profile observed for all nitrate systems, i.e. an induction period and a fast reaction stage followed by a steady residual 'plateau' concentration of hydrazine. Above this ionic strength, the hydrazine oxidation profile changes, resulting in a steady decline in hydrazine concentration at the end of the fast reaction stage. The results obtained can therefore be divided into two groups, namely, those which display the 'normal' nitrate-type kinetics, Figure 3.4, and those which display a continual loss of hydrazine over the 25 hour span of the reaction, Figure 3.5.

As the concentration of perchlorate ion is increased, and hence also the ionic strength, the initiation period decreases in length. This is accompanied by an increase in the rate of the fast reaction stage

Figure 3.4 : The Effect of Increasing Perchlorate Ion Concentration and Ionic Strength on the Oxidation of Hydrazine over a 25 hour period : Range of Ionic Strength 0.9 - 3.0 mol dm^{-3}

[Tc]	:	1.6 x 10^{-3} mol dm^{-3}
[$N_2H_5NO_3$]	:	0.1 mol dm^{-3}
[$NaNO_3$]	:	0.3 mol dm^{-3}
[$HClO_4$]	:	0.5 mol dm^{-3}
[$NaClO_4$]	:	0.0 - 2.7 mol dm^{-3}
Temp.	:	35°C

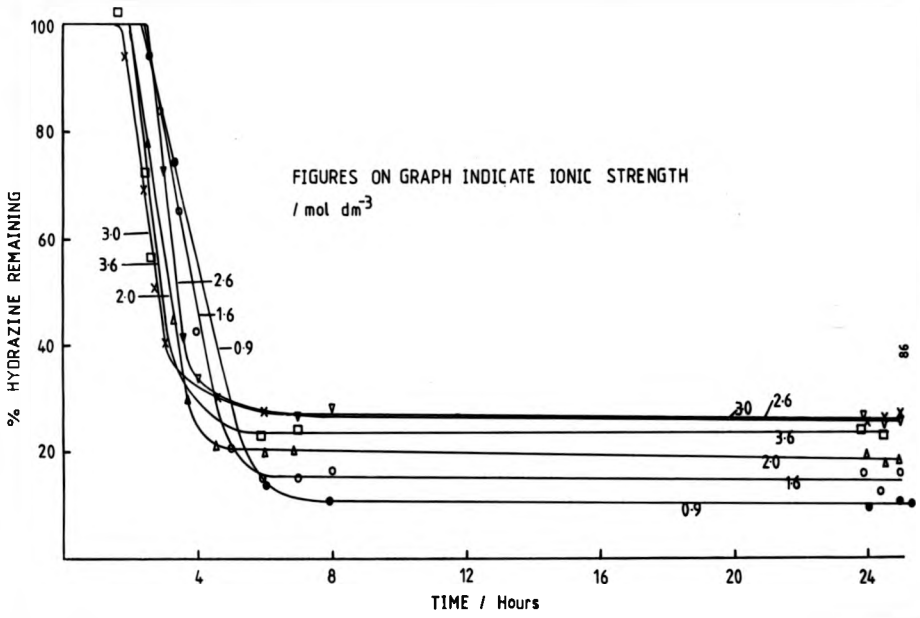
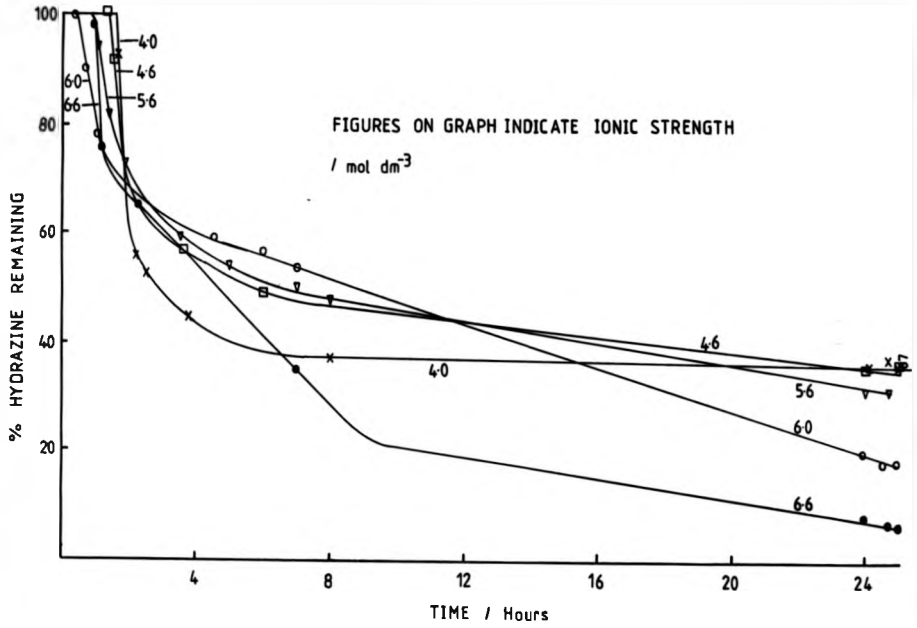

100
80
60
40
20
% HYDRAZINE REMAINING
FIGURES ON GRAPH INDICATE IONIC STRENGTH
/ mol dm^{-3}
3·0
3·6
2·0
2·6
1·6
0·9
4
8
12
16
20
24
TIME / Hours

Figure 3.5 : The Effect of increasing Perchlorate Ion Concentration and Ionic Strength on the Oxidation of Hydrazine over a 25 Hour Period : Range of Ionic Strength 4.0 - 6.6 mol dm^{-3}

[Tc]	:	1.6 x 10^{-3} mol dm^{-3}
[$N_2H_5NO_3$]	:	0.1 mol dm^{-3}
[$NaNO_3$]	:	0.3 mol dm^{-3}
[$HClO_4$]	:	0.5 mol dm^{-3}
[$NaClO_4$]	:	3.1 - 5.7 mol dm^{-3}
Temp.	:	35°C


100
80
60
40
20
% HYDRAZINE REMAINING
4·0
4·6
5·6
6·0
6·6
FIGURES ON GRAPH INDICATE IONIC STRENGTH
/ mol dm⁻³
4
8
12
16
20
24
TIME / Hours

(up to μ = 4.6 mol dm^{-3}) and an increase in the residual amount of hydrazine remaining as a result of the termination reaction.

For the range of higher ionic strengths, however, whilst the initiation period continues its trend of decreasing in length, the rate of the fast reaction stage begins to decrease. This is accompanied by the disappearance of a steady residual concentration of hydrazine on cessation of the reaction. It appears that in this region of sodium perchlorate concentration, a wholly new situation obtains as far as the chain reaction is concerned. This is confirmed when the rate of oxidation of hydrazine during the fast reaction stage is plotted against increasing ionic strength (Figure 3.6). It is clearly evident that there is a sharp maximum in the dependence on ionic strength (or ratio of perchlorate to nitrate ion concentrations at *ca.* 4.5 mol dm^{-3}. Above this figure the rate of the fast reaction stage declines sharply with further increases in perchlorate ion concentration.,

The time-evolution of the production of ammonium ions shows close similarities to that of the oxidation of hydrazine, as expected (Figure 3.7). For ionic strengths up to μ = 4.6 mol dm^{-3} a fast reaction period is observed followed by a steady state concentration of ammonium ions. Above this perchlorate ion concentration no 'plateau' concentration of ammonium ions is observed and instead a continued slow production takes place, in parallel with the continuing hydrazine oxidation.

Figure 3.8 illustrates the effect of perchlorate ion concentration on the rate of production of ammonium ions. A steady decrease in the reaction rate is observed (rather than the appearance of a maximum), which is accompanied by a decrease in the percentage yield of ammonia, Table 3.1. Thus one effect of attempting to increase

Figure 3.6 : Rate of Hydrazine Oxidation during the Fast Reaction Stage with increasing Ionic Strength

[Tc]	:	1.6 x 10^{-3} mol dm^{-3}
$[N_2H_5NO_3]$	:	0.1 mol dm^{-3}
$[NaNO_3]$	:	0.3 mol dm^{-3}
$[HClO_4]$	:	0.5 mol dm^{-3}
$[NaClO_4]$	:	0.0 - 5.7 mol dm^{-3}
Temp.	:	35°C

RATE OF HYDRAZINE OXIDATION (During Fast Reaction) / $\times 10^{-5}$ mol dm^{-3} s^{-1}
2·0
1·6
1·2
0·8
0·4
1
2
3
4
5
6
μ / mol dm^{-3}

Figure 3.7 : The Effect of increasing Perchlorate Ion Concentration and Ionic Strength on Ammonium Ion Production over a 25 hour period : Range of Ionic Strength 1.6 - 6.1 mol dm^{-3}

[Tc]	:	1.6 x 10^{-3}
$[N_2H_5NO_3]$	:	0.1 mol dm^{-3}
$[NaNO_3]$	:	0.3 mol dm^{-3}
$[HClO_4]$	:	0.5 mol dm^{-3}
$[NaClO_4]$	:	0.7 - 5.2 mol dm^{-3}
Temp.	:	35°C

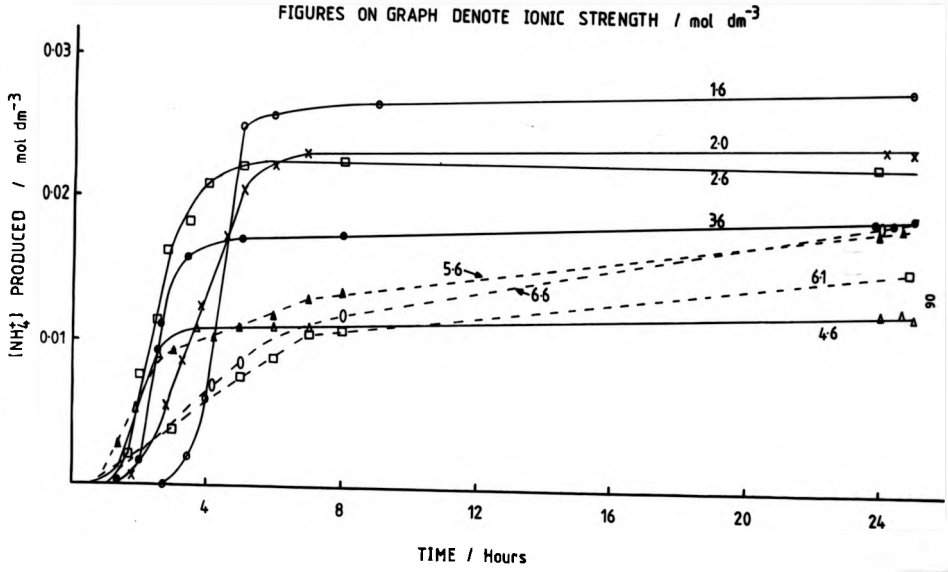

FIGURES ON GRAPH DENOTE IONIC STRENGTH / mol dm^{-3}
0·03
0·02
0·01
[NH$_4^+$] PRODUCED / mol dm^{-3}
1·6
2·0
2·6
3·6
5·6
6·6
6·1
4·6
0
0
0
4
8
12
16
20
24
TIME / Hours

Figure 3.8 : Dependence of the Rate of Production of Ammonium Ion on Ionic Strength

[Tc]	:	1.6×10^{-3} mol dm^{-3}
$[N_2H_5NO_3]$	:	0.1 mol dm^{-3}
$[NaNO_3]$	:	0.3 mol dm^{-2}
$[HClO_4]$	:	0.5 mol dm^{-3}
$[NaClO_4]$	:	0.0 - 5.7 mol dm^{-3}
Temp.	:	35°C

RATE OF AMMONIUM ION PRODUCTION (During Fast Reaction) / $\times 10^{-6}$ mol dm^{-3} s^{-1}
5
4
3
2
1
1
2
3
4
5
6
μ / mol dm^{-3}

Table 3.1 : Dependence of the Percentage Yield of Ammonium Ions on Ionic Strength ($NaClO_4$)

Ionic Strength /mol dm^{-3}	$[NH_4^+]$ Produced /mol dm^{-3}	$[N_2H_4]$ Oxidised /mol dm^{-3}	Yield of NH_4^+ /mole %
1.6	0.0567	0.0853	66.5
2.0	0.0547	0.0812	67.4
2.6	0.0430	0.0743	57.9
3.0	0.0315	0.0739	42.6
3.6	0.0185	0.0765	50.6
4.6	0.0128	0.0646	39.2
6.0	0.0298	0.0805	37.0
6.6	0.0362	0.0928	39.0

the ionic strength by adding sodium perchlorate is to inhibit those reactions leading to the production of ammonium ions. It is possible to explain the changing profile of the hydrazine oxidation for the range of ionic strengths studied in terms of changes in the rates of the initiation, fast reaction and termination reactions. These changes are brought about because the addition of perchlorate does not merely change μ, but instigates an entirely new cycle of reactions. The effect of ionic strength may be highly significant at μ up to 3 or 4 mol dm^{-3}, but above this point a new set of reactions involving perchlorate are introduced.

For ionic strengths of greater than 4 mol dm^{-3}, the length of the fast reaction stage is reduced and the sudden changeover from the fast reaction to the termination reaction stage observed in nitrate media is replaced instead by a steady fall in hydrazine concentration. From this it can be inferred that the rate of oxidation of Tc^{VI} by perchlorate ion is less than that by nitrate ion resulting in a slower termination reaction, and that the rate of oxidation of Tc^{IV} to Tc^{VI} by perchlorate is slower than the similar reaction involving nitrate. This would result in a gradual production of Tc^{VI} which would react much more rapidly with hydrazine than with perchlorate ion, thus explaining the observed slow oxidation stage of hydrazine in place of the termination stage.

3.3 The Technetium-Hydrazine Reaction in Mixed Nitric Acid - Hydrochloric Acid Systems

The effects of adding low concentrations of hydrochloric acid (up to 0.1 mol dm^{-3}) to the $Tc-N_2H_4-HNO_3$ reaction mixtures was investigated to see whether the addition of chloride ions would exert any effect on the reaction kinetics. Three such trial reactions were carried out, two containing both hydrochloric acid and nitric acids and a 'blank' solution containing only nitric acid (4.0 mol dm^{-3}). The hydrazine oxidation profiles for these three reaction mixtures are illustrated in Figure 3.9

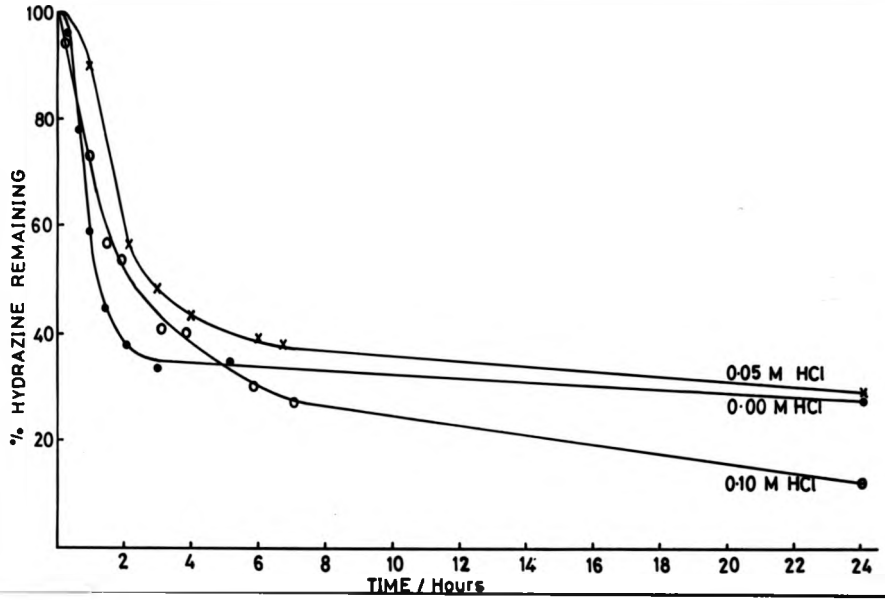
The blank reaction mixture containing 4.0 mol dm^{-3} nitric acid displays the typical kinetics for a nitrate system. The addition of HCl (0.05 mol dm^{-3}) however has a dramatic effect on the hydrazine oxidation profile, effecting a decrease in the rate of the fast reaction with a more gradual appearance of the termination reaction.

The situation induced by the addition of HCl at 0.1 mol dm^{-3} concentration displays even greater deviations from 'normal' behaviour, with a shortened fast reaction stage followed by a gradual levelling off in reaction rate. The clear 'plateau' concentration of hydrazine is absent and has been replaced by a continual, although very slow, further consumption of hydrazine.

From this it is evident that chloride ion has a marked effect on the reaction kinetics. This is very probably due to its complexation with technetium to yield oxychlorotechnetium complexes which display different reactivities from the technetium -oxo complexes involved in the all-nitrate systems.

Figure 3.9 : Time Profiles for the Oxidation of Hydrazine in Mixed Nitric Acid - Hydrochloric Acid Systems

[Tc]	:	1.6×10^{-3} mol dm^{-3}
$[N_2H_5NO_3]$	:	0.1 mol dm^{-3}
$[HNO_3]$	:	4.0 mol dm^{-3}
[HCl]	:	0.05 - 0.1 mol dm^{-3}
Temp.	:	$35^{o}C$


100
80
60
40
20
% HYDRAZINE REMAINING
2
4
6
8
10
12
14
16
18
20
22
24
TIME / Hours
0·05 M HCl
0·00 M HCl
0·10 M HCl

3.4 Conclusions

An investigation into the effects of nitrate ions on the reaction kinetics, using perchloric acid and with its sodium salt to maintain a constant ionic strength, showed that the nitrate ion has little effect on the initiation reaction. As the concentration of nitrate ion is raised, the rate of hydrazine oxidation during the fast reaction stage increases, however, the rate of production of ammonium ions falls.

Solutions which contained greater than 2.5 mol dm^{-3} nitrate ion exhibited a 'normal' hydrazine oxidation kinetic profile for a nitrate system, i.e. a stage of rapid hydrazine destruction followed by a rapid termination of the reaction to leave a 'plateau' concentration of hydrazine. However, below 2.5 mol dm^{-3} nitrate ion concentration, the 'plateau' concentration is replaced instead by a stage of more gradual hydrazine oxidation which continues for over 24 hours. Reaction mixtures containing high perchlorate ion concentrations invariably exhibited this gradual oxidation stage, due to the introduction of a modified cycle of reactions.

The effects of ionic strength on the kinetics of hydrazine oxidation were investigated by adding increasing amounts of sodium perchlorate to reaction mixtures. It was found that for ionic strengths up to 4.0 mol dm^{-3} the rate of hydrazine oxidation during the fast reaction stage was increased. Above this ionic strength, the rate of the fast reaction stage underwent a rapid decline. It is considered that the initial increase in the rate of hydrazine oxidation is due to the increasing ionic strength. However, at a certain point the reactions instigated by the perchlorate ion become more prominent and lead to an inhibition of the rate of hydrazine oxidation.

The addition of low concentrations (up to 0.1 mol dm^{-3}) of

hydrochloric acid to $Tc-N_2H_4-HNO_3$ reaction mixtures showed that whilst there was no significant effect on the length of the initiation stage, the length of the fast reaction stage was substantially decreased. This effect was accompanied by a gradual decline in the rate of hydrazine oxidation, leading to a stage of slow hydrazine loss from the solutions which continued for over 24 hours. Thus these solutions exhibited the typical kinetics of hydrazine oxidation seen in solutions containing low nitrate concentrations and high perchlorate concentrations. This similarity is regarded as due to the presence of chloride in both systems which will complex the technetium to form species of differing reactivity.

4. The Technetium-Hydrazine Reaction In Perchlorate Media

The reduction of pertechnetate ions by hydrazine in perchloric acid solutions has been studied previously using U.V.-visible spectroscopy by Spitsyn et al. (16). They employed perchloric acid rather than nitric acid as the latter absorbs light in the U.V. part of the spectrum, thus obscuring the absorption peaks due to the pertechnetate ion. After the end of the initiation period they observed that the solution became brown, λ_{max} 260 nm, and absorbed light over the entire measured range of the spectrum (190-800 nm). This general observation was supported by our own observations using U.V.-visible spectroscopy.

Perchloric acid has also been utilised in two studies by Suslov et al. (38, 119). In their first publication (119) they dealt with the kinetics of Pu^{III} oxidation by Tc^{VI} ions, and in their second publication they covered the kinetics of the oxidation of Pu^{III} by hydrogen peroxide in the presence of Tc^{VI} in nitric acid-perchloric acid mixtures. Whilst these two papers do not deal with hydrazine oxidation, they are of interest as they present a detailed study of the reduction of Tc^{VI}.

The point of interest to make is that of these three studies, only that by Spitsyn et al. (16) employed a nitrate-free system, what they failed to comment on was the surprising fact that the Tc-hydrazine reaction occurs at all in an all-perchlorate system.

The only other publication we found that covers the reaction between pertechnetate and hydrazine in perchlorate media is that due to Gorski and Koch (120), who state that hydrated technetium dioxide is the final reaction product. Our results confirm this as we observed the production of large amounts of TcO_2 in systems containing less than 1.0 mol dm^{-3} $HClO_4$, with an ionic strength of 1.1 mol dm^{-3}.

We have investigated the kinetics of the reactions that occur in perchlorate media by assaying the concentrations of hydrazine, ammonium ions, Tc^{IV} and Tc^{V}. We have also studied the reduction of the pertechnetate ion by hydrazine in solutions of varying perchloric acid concentration using U.V.-visible spectroscopy. Attempts have also been made to correlate spectral changes with changes in the concentrations of Tc^{IV} and Tc^{V}.

Electron spin resonance studies have also been conducted in order to ascertain the nature of the coloured, paramagnetic technetium complexes that are formed during the course of the reaction.

4.1 The Technetium-Hydrazine Reaction in Perchlorate Media with an Ionic Strength of 1.1 mol dm^{-3}

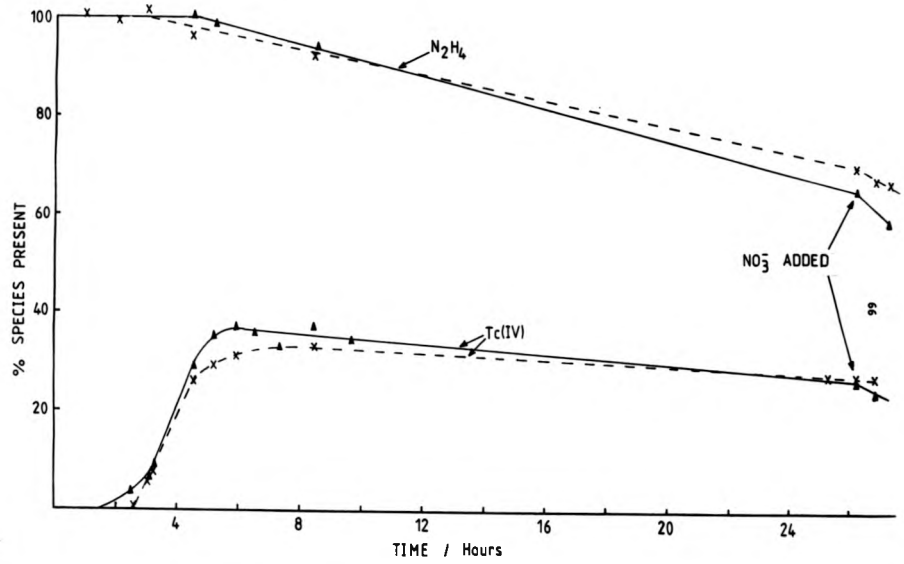
The oxidation of hydrazine in 1.0 mol dm^{-3} perchloric acid solutions takes place very slowly and typically exhibits an initiation period of about 4 hours at 35°C with [Tc] = 1.6×10^{-3} mol dm^{-3} and $[N_2H_4]$ = 0.1 mol dm^{-3}. Reaction mixtures were assayed for their hydrazine, ammonium ion and Tc^{IV} and Tc^{V} content, most reactions being followed over a 28 hours period, although two were followed for 37 hours.

In all cases, as a means of investigating the greater effectiveness of nitrate ion as an oxidant, compared to perchlorate, an aliquot of a concentrated sodium nitrate solution was added to the reaction mixtures 15 or 26 hours after initiation.

The profiles of hydrazine oxidation and Tc^{IV} production for duplicate experiments are illustrated in Figure 4.1. After an initiation period of about 4 hours, the oxidation of hydrazine proceeds slowly and at a steady rate with no indication of the fast reaction period typical of the nitrate ion system. The sudden

Figure 4.1: The Destruction of Hydrazine and the Evolution of Tc^{IV} and Tc^{V} with Time in Perchlorate Media.

[Tc]	:	1.6×10^{-3} mol dm^{-3}
$[N_2H_4]$	:	0.1 mol dm^{-3}
$[HClO_4]$	:	1.0 mol dm^{-3}
Temp	:	$35^{o}C$
$NaNO_3$	:	0.29 mol dm^{-3}


100
80
60
40
20
% SPECIES PRESENT
N_2H_4
NO_3^- ADDED
99
Tc(IV)
4
8
12
16
20
24
TIME / Hours

increase in the rate of hydrazine oxidation after 26 hours is due to the addition of a small aliquot of sodium nitrate solution.

The profile of technetium(IV) production shows a sudden increase in the concentration of Tc^{IV} some time before the end of the initiation period. The reason for this apparent discrepancy is due to the very small fraction of the hydrazine utilized to produce a significant quantity of Tc^{IV}.

The reaction mixtures, which were initially colourless, became a very pale yellow colour after 2-3 hours. However, when the concentration of Tc^{IV} rapidly increased they became brown and then opaque due to the formation of a black precipitate. The filtration of small quantities of these turbid solutions yielded a black precipitate regarded as TcO_2 and a clear yellow solution which contained a Tc^{IV} complex.

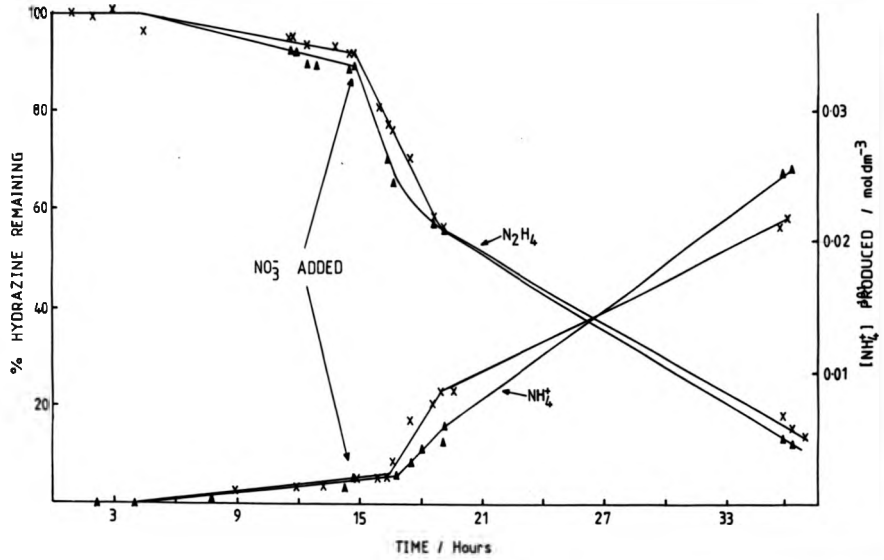
After reaching a peak concentration, the amount of Tc^{IV} then slowly declined showing that a species capable of oxidising Tc^{IV} is present in the system. On adding nitrate to the reaction mixtures, the concentration of Tc^{IV} began to fall more rapidly as it was oxidised presumably to Tc^{VI}. This sudden production of Tc^{VI} in the system caused a prompt increase in the rate of hydrazine oxidation.

Figure 4.2 illustrates the results for ammonium ion production and hydrazine oxidation for a second pair of duplicate reactions. As with Figure 4.1, an initiation period of about 4 hours occurs, after which the concentration of hydrazine begins to fall slowly. This is accompanied by a slow production of ammonium ions, and the formation of a black precipitate of TcO_2.

After 15 hours an aliquot of sodium nitrate solution was added; this resulted in an immediate decline in the concentration of hydrazine. Surprisingly however a time lag of approximately 1.5 hours is

Figure 4.2: The Destruction of Hydrazine, Evolution of Tc^{IV} and Tc^{V} and Production of Ammonium Ions with Time in Perchlorate Media.

[Tc]	:	1.6×10^{-3} mol dm^{-3}
$[N_2H_4]$	:	0.1 mol dm^{-3}
$[HClO_4]$	:	1.0 mol dm^{-3}
Temp	:	35°C
$[NaNO_3]$	:	0.29 mol dm^{-3}


100
80
60
40
20
% HYDRAZINE REMAINING
0·03
0·02
0·01
[NH$_4^+$] PRODUCED / mol dm^{-3}
N_2H_4
NO_3^- ADDED
NH_4^+
3
9
15
21
27
33
TIME / Hours

observed before a rapid rise in the rate of production of ammonium ions occurs. After a short 'fast reaction' stage, the rate of formation of ammonia slows down in line with a similar decrease in the rate of oxidation of hydrazine.

Thus, it can be seen that the addition of a small amount of nitrate to these solutions enables the almost complete oxidation of hydrazine to take place. The continuing oxidation of hydrazine at the end of the fast reaction stage will be due partly to the gradual reoxidation of the precipitated Tc^{IV} to a species which can react further with hydrazine and also due to the termination reaction being rendered ineffective by the low concentration of oxidants in the solution which results in the continued loss of hydrazine.

4.2 The Effect of Perchloric Acid Concentration on the Technetium-Hydrazine Reaction in Perchlorate Media with an Ionic Strength of 7.0 mol dm^{-3}

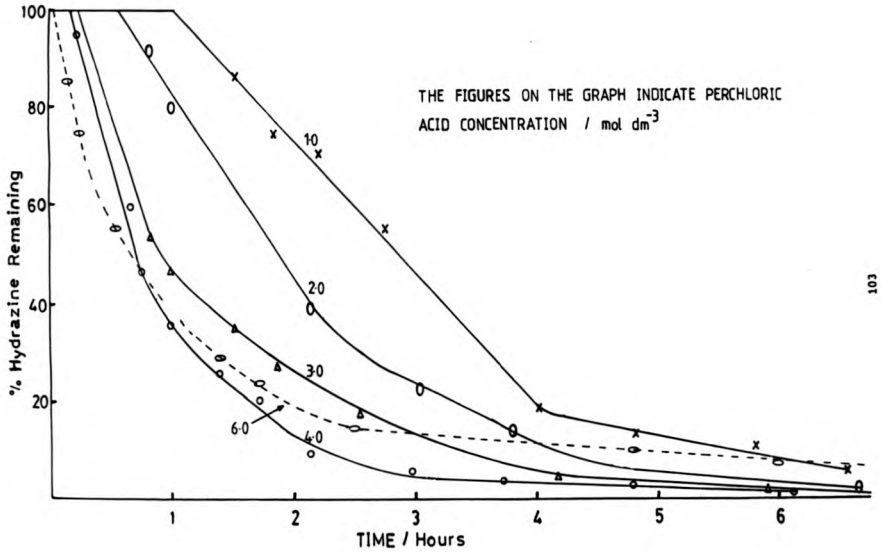
The unexpected observations detailed in Section 4.1 that demonstrated the role of perchloric acid and the perchlorate ion in the technetium-hydrazine reaction necessitated further investigation of the kinetics of the reactions that occur in perchlorate media.

It was found that by increasing the concentration of perchlorate ions in reaction mixtures from 1.0- to 7.0 mol dm^{-3} the rate of oxidation of hydrazine was greatly increased and that the reaction proceeded to complete destruction of the hydrazine.

In order to investigate the effects of acidity on the reaction rate, a series of experiments were conducted in which the concentration of perchloric acid was varied from 1.0 to 6.0 mol dm^{-3}. The profile of the varying concentration of hydrazine with time with increasing acidity is given in Figure 4.3; for the sake of clarity the results

Figure 4.3: The Effects of Altering the Perchloric Acid Concentration on the Tc-catalysed Oxidation of Hydrazine in Perchlorate Media

[Tc]	:	1.6×10^{-3} mol dm^{-3}
$[N_2H_4]$	:	0.1 mol dm^{-3}
$[HClO_4]$	:	Varied
$[NaClO_4]$	:	Varied
$[ClO_4^-]_{Total}$	:	6.9 mol dm^{-3}
Temp	:	35^oC


THE FIGURES ON THE GRAPH INDICATE PERCHLORIC ACID CONCENTRATION / mol dm^{-3}
% Hydrazine Remaining
TIME / Hours
100
80
60
40
20
1
2
3
4
5
6
1·0
2·0
3·0
4·0
6·0

for the 5.0 mol dm^{-3} perchloric acid system have been omitted. The solutions were also assayed for their Tc^{V} and Tc^{IV} content and Figure 4.4 gives the changing concentrations of Tc^{IV} with time; as with Figure 4.3 the results for the 5.0 mol dm^{-3} $HClO_4$ system have been omitted.

The profiles of the changing concentration of Tc^{V} closely paralleled those for Tc^{IV}, the peak concentration of Tc^{V} being reached at the same time as the sharp spike in the production of Tc^{IV}. The yields of Tc^{V} were found to be acid-dependent, with an almost 10% peak production in 6.0 mol dm^{-3} acid and only 2 - 3% in 1.0 mol dm^{-3}.

The dependence of the rate of oxidation of hydrazine upon acidity is presented in Figure 4.5. It can be seen that the reaction exhibits a linear dependence on acidity with the rate of hydrazine oxidation approximately doubling as the acidity is doubled. Thus the situation in perchloric acid differs sharply from that in nitric acid; in perchloric acid the rate of the fast reaction stage is acid-dependent whilst in HNO_3 the major effect of acidity is to inhibit the rate of oxidation of hydrazine during the fast reaction stage by promoting the termination reaction.

4.3 The Use of U.V.-Visible Spectroscopy to Monitor Variation in the Rate of Pertechnetate Ion Reduction with Perchloric Acid

The rate of reduction of pertechnetate ion in the Tc-hydrazine reaction was followed by monitoring changes in the absorbance of the solution at 244.7 nm. (λ_{max} TcO_4^-; doublet peak at 244.5 and 247.8 nm, broad peak at 287.7 nm).

The plots of absorbance at 244.7 nm versus time typically displayed a period of slow pertechnetate reduction, which decreased in length as the acidity was raised. This was followed by a period of fast

Figure 4.4: Variations in the Concentration of Tc^{IV} with Time with Increasing Concentration of Perchloric Acid

[Tc]	:	1.6×10^{-3} mol dm^{-3}
$[N_2H_4]$	:	0.1 mol dm^{-3}
$[HClO_4]$	:	Varied
$[NaClO_4]$	:	Varied
$[ClO_4^-]_{Total}$	:	6.9 mol dm^{-3}
Temp	:	35°C

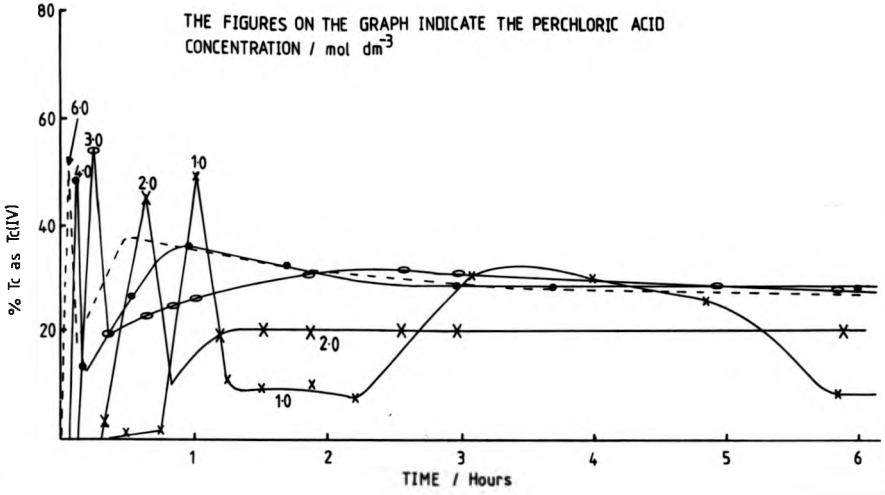

THE FIGURES ON THE GRAPH INDICATE THE PERCHLORIC ACID CONCENTRATION / mol dm^{-3}
% Tc as Tc(IV)
TIME / Hours
6·0
3·0
4·0
2·0
1·0
2·0
1·0
80
60
40
20
1
2
3
4
5
6

Figure 4.5: Variation in the rate of Oxidation of Hydrazine during the Fast Reaction Stage with Perchloric Acid Concentration

[Tc]	:	1.6×10^{-3} mol dm^{-3}
$[N_2H_4]$	:	0.1 mol dm^{-3}
$[HClO_4]$	:	Varied
$[NaClO_4]$	:	Varied
$[ClO_4^-]_{Total}$	:	6.9 mol dm^{-3}
Temp	:	35^oC

Rate of Hydrazine Destruction (Fast Reaction) / × 10⁻⁵ mol dm⁻³ s⁻¹
1
2
3
4
1
2
3
4
5
6
[H⁺] / mol dm⁻³

reduction, the rate of which increased with increasing acidity; thereafter the absorbance increased due to interference from a neighbouring peak.

It was found that the length of the initial slow reduction stage of TcO_4^- corresponded well with that of the initiation period observed for hydrazine oxidation, and also that the stage of fast reduction of pertechnetate occurs during the so-called 'fast reaction' stage of hydrazine destruction.

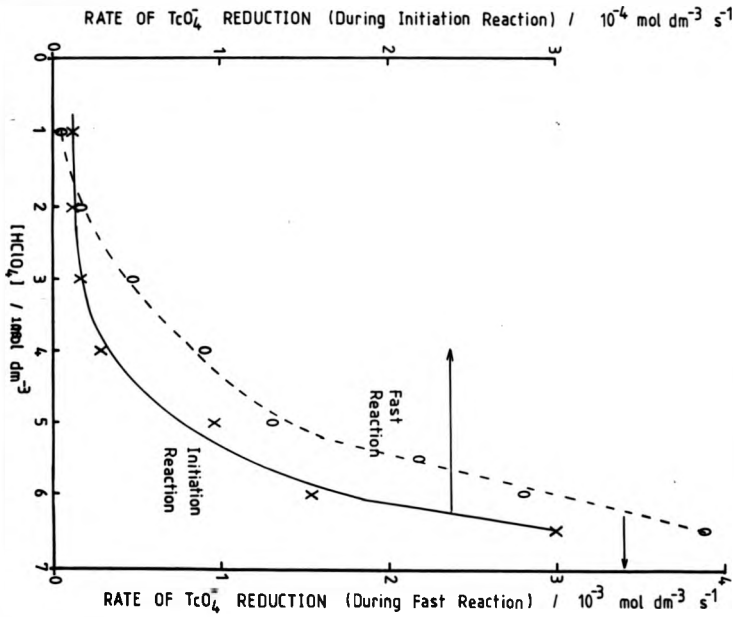
The gradients of the slopes during each of these two stages were determined; the acid-dependences of the rates of these reactions are presented in Figure 4.6.

From this figure it can be seen that the rate of pertechnetate reduction during the fast reaction stage is proportional to the square of acid concentration. Whilst the rate of TcO_4^- reduction during the initial stage of the reaction displays no acid dependence below 2.5 mol dm^{-3} perchloric acid, thereafter it is approximately dependent on the square of acid concentration.

This continued reduction of pertechnetate well into the fast reaction stage contrasts with the situation observed in nitric acid by Garraway and Wilson (15) who found the fast reaction stage commences when the concentration of pertechnetate ion has been substantially reduced. Clearly in perchloric acid a somewhat different regime operates which enables the system to enter the fast reaction stage when only partial reduction of pertechnetate has occurred.

Figure 4.6: Rate of Reduction of Pertechnetate Ion during the Initial and Fast Reaction Stages of Hydrazine Oxidation versus Perchloric Acid Concentration

[Tc]	:	1.6×10^{-3} mol dm^{-3}
$[N_2H_4]$	:	0.1 mol dm^{-3}
$[HClO_4]$	:	Varied
$[NaClO_4]$	:	Varied
$[ClO_4^-]_{Total}$	:	6.9 mol dm^{-3}
Temp	:	23^oC


RATE OF TcO_4^- REDUCTION (During Initiation Reaction) / 10^{-4} mol dm^{-3} s^{-1}
[HClO$_4$] / mol dm^{-3}
Initiation Reaction
Fast Reaction
RATE OF TcO_4^- REDUCTION (During Fast Reaction) / 10^{-3} mol dm^{-3} s^{-1}

4.4 The Effect of Temperature on the Kinetics of the Tc-Hydrazine Reaction in Perchlorate Media

The effect of increasing temperature on the kinetics of hydrazine oxidation and of ammonium ion production was investigated in a system containing perchloric acid (2.0 mol dm^{-3}) sodium perchlorate (4.9 mol dm^{-3}), pertechnetate ion (1.6 x 10^{-3} mol dm^{-3}) and hydrazine (0.1 mol dm^{-3}).

The time-profile of hydrazine oxidation for various temperatures is illustrated in Figure 4.7. It is clearly evident that as the temperature is increased, the length of the initiation period decreases and the rate of hydrazine oxidation during the fast reaction stage increases markedly. Thus at 50°C complete destruction of hydrazine is observed after 1.5 hours, but at 35°C a period of 6.5 hours is required; below this temperature very slow loss of hydrazine is observed after the end of the fast reaction stage, with over 20% remaining after 7 hours at 27.7°C.

The time-profiles of production of ammonium ions at various temperatures display generally similar behaviour (Figure 4.8). The percentage yield of ammonia, however, remains unaffected by changes in temperature and stays at about 10%,.

For both hydrazine loss and ammonium production plots of ln (rate of fast reaction stage) versus 1/T(K) are linear (Figures 4.9 and 4.10), yielding activation energies for the rate-determining steps of 35.5 ± 1 kJ mol^{-1} and 83 ± 12 kJ mol^{-1} respectively. This can be compared with the value of 72±6 kJ mol^{-1} obtained by Garraway and Wilson (27) for the nitrate system. For our reaction in perchlorate media, however, the slow step is probably the oxidation of Tc^{IV} by ClO_4^- which appears to be characterised by a much lower energy requirement than the similar reaction involving nitrate.

Figure 4.7: The Effects of Increasing Temperature on the Kinetics of Hydrazine Oxidation with Time in Perchlorate Media

[Tc]	:	1.6 x 10^{-3} mol dm^{-3}
[N_2H_4]	:	0.1 mol dm^{-3}
[$HClO_4$]	:	2.0 mol dm^{-3}
[$NaClO_4$]	:	4.9 mol dm^{-3}
Temp	:	Varied

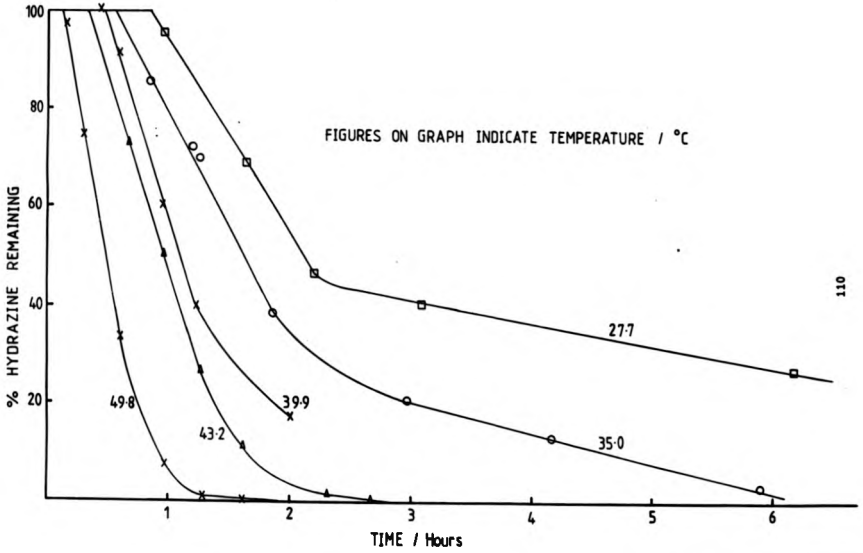

100
80
60
40
20
% HYDRAZINE REMAINING
FIGURES ON GRAPH INDICATE TEMPERATURE / °C
27·7
39·9
43·2
49·8
35·0
1
2
3
4
5
6
TIME / Hours

Figure 4.8: The Effects of Increasing Temperature on the Kinetics of Ammonium Ion Production with Time in Perchlorate Media

[Tc]	:	1.6×10^{-3} mol dm^{-3}
$[N_2H_4]$	:	0.1 mol dm^{-3}
$[HClO_4]$	:	2.0 mol dm^{-3}
$[NaClO_4]$	:	4.9 mol dm^{-3}
Temp	:	Varied

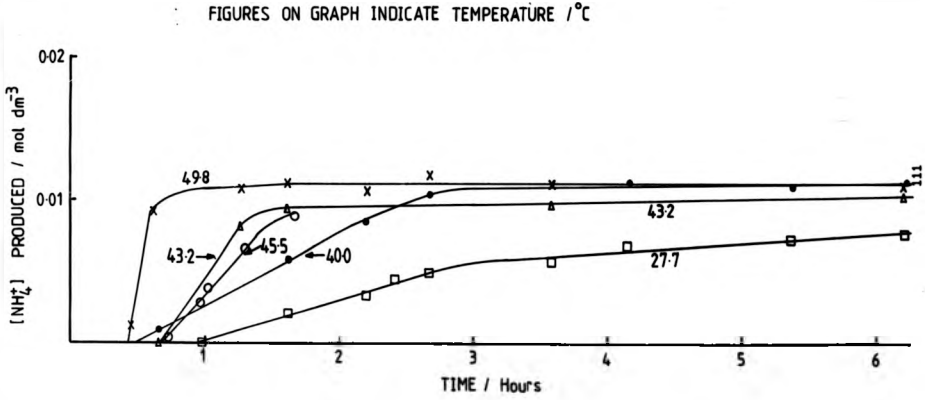

FIGURES ON GRAPH INDICATE TEMPERATURE /°C
0·02
0·01
[NH$_4^+$] PRODUCED / mol dm^{-3}
49·8
43·2
45·5
40·0
43·2
27·7
1
2
3
4
5
6
TIME / Hours

Figure 4.9: In(Rate) of Hydrazine Oxidation during Fast Reaction Stage versus Reciprocal Temperature

[Tc]	:	1.6 x 10^{-3} mol dm^{-3}
$[N_2H_4]$	:	0.1 mol dm^{-3}
$[HClO_4]$	:	2.0 mol dm^{-3}
$[NaClO_4]$	:	4.9 mol dm^{-3}
Temp	:	Varied

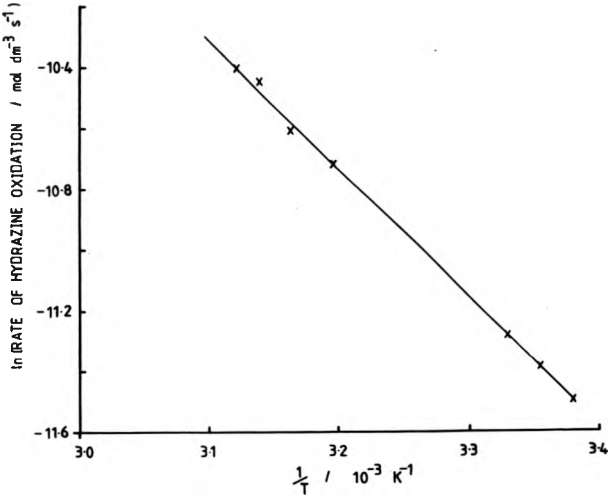
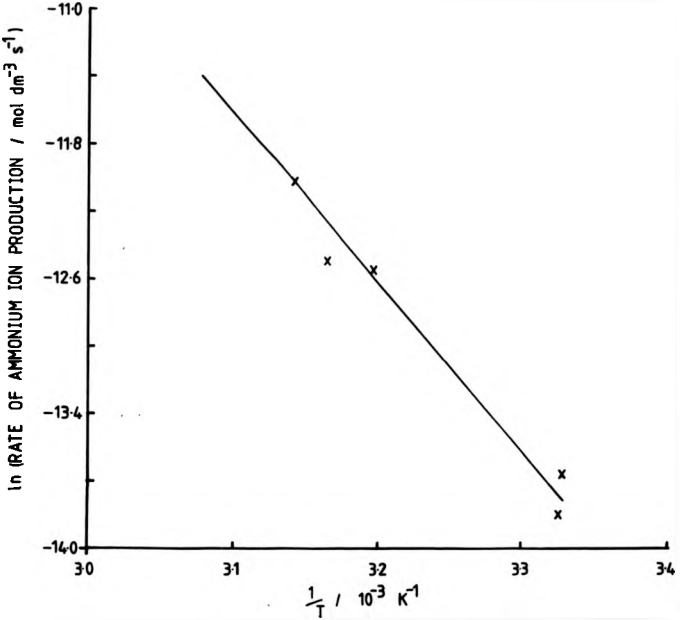

ln (RATE OF HYDRAZINE OXIDATION / mol dm^{-3} s^{-1})
-10·4
-10·8
-11·2
-11·6
3·0
3·1
3·2
3·3
3·4
$\frac{1}{T}$ / 10^{-3} K^{-1}

Figure 4.10 : ln(Rate) of Production of Ammonium Ions during Fast Reaction Stage versus Reciprocal Temperature

[Tc]	:	1.6×10^{-3} mol dm^{-3}
$[N_2H_4]$	:	0.1 mol dm^{-3}
$[HClO_4]$	:	2.0 mol dm^{-3}
$[NaClO_4]$	:	4.9 mol dm^{-3}
Temp	:	Varied


ln (RATE OF AMMONIUM ION PRODUCTION / mol dm^{-3} s^{-1})
-11·0
-11·8
-12·6
-13·4
-14·0
3·0
3·1
3·2
3·3
3·4
$\frac{1}{T}$ / 10^{-3} K^{-1}

4.5 The Effects on Reaction Kinetics of adding Chlorate and Hypochlorite Ions to Tc-N_2H_4 Solutions in Perchlorate Media.

We found that during the Tc-catalysed oxidation of hydrazine by the perchlorate ion, the latter is reduced in successive steps to chloride ion. Attempts were therefore made, using a variety of spectrophotometric assays, to determine the amounts of other oxychloro species present in the solution.

Unfortunately, due to the mutual interference of these ions, particularly in the presence of large excesses of perchlorate ion, no meaningful results could be obtained.

Although it proved impossible to determine the amounts of each of these ions in solution simultaneously, the necessity of investigating their effects on the reaction kinetics remained.

4.5.1 Effect of Addition of Chlorate Ion

The effects of adding potassium chlorate on the rate of oxidation of hydrazine and on the concentrations of Tc^{IV} and Tc^{V} present in duplicate solutions during the fast reaction stage of the Tc-hydrazine reaction in perchloric acid (2.0 mol dm^{-3}, $[ClO_4^-]_{Total}$ = 6.9 mol dm^{-3}) were investigated.

The reaction mixtures were initiated in the normal way by adding an aliquot of a concentrated hydrazine solution; after 1 hour 29 minutes, when the reaction had entered the so-called fast reaction stage, an aliquot of potassium chlorate solution was added to both solutions. The hydrazine oxidation profile, together with that of Tc^{IV}, is presented in Figure 4.11. It can be seen that the addition of chlorate ion to the solution causes a very rapid termination of the reaction, due to the oxidation of the Tc^{IV}. Figure 4.12 shows the evolution of Tc^{IV} and Tc^{V} under the normal reaction conditions

Figure 4.11 : The Effects on the Oxidation of Hydrazine and Tc^{IV} Concentration of Adding Chlorate Ion to a $Tc\text{-}N_2H_4\text{-}HClO_4$ Reaction Mixture

[Tc]	:	1.6×10^{-3} mol dm^{-3}
$[N_2H_4]$	:	0.1 mol dm^{-3}
$[HClO_4]$	:	2.0 mol dm^{-3}
$[NaClO_4]$	:	4.9 mol dm^{-3}
$[KClO_3]$	:	0.01 mol dm^{-3}
Temp	:	35^oC

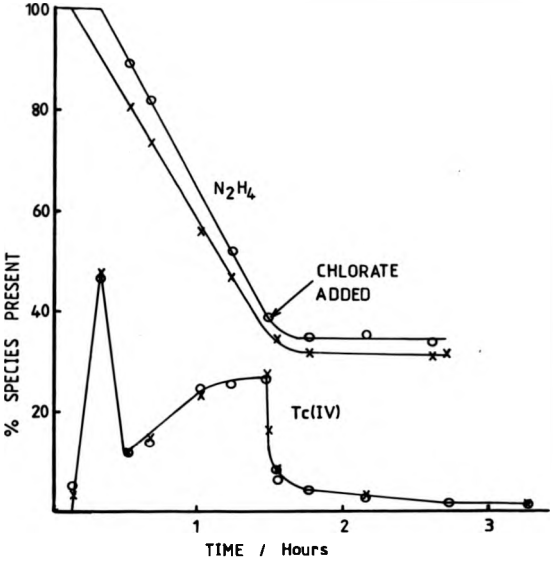
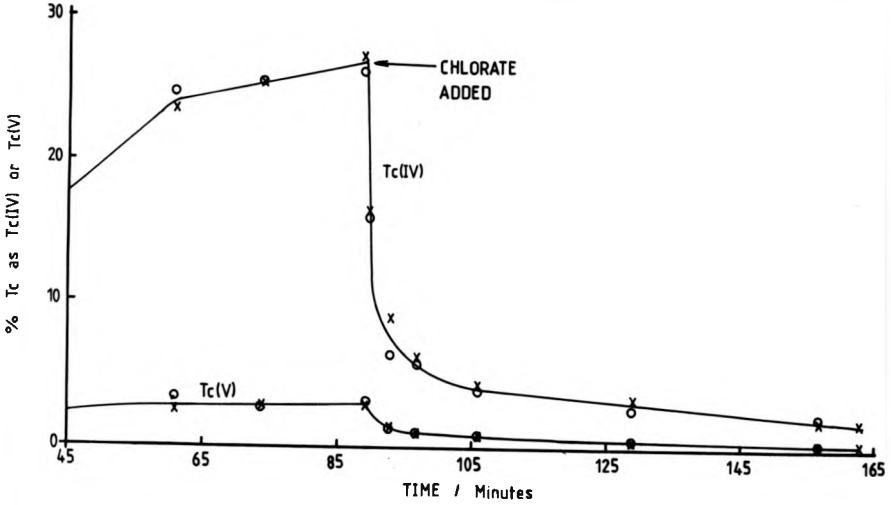

100
80
60
40
20
% SPECIES PRESENT
N_2H_4
CHLORATE
ADDED
Tc(IV)
1
2
3
TIME / Hours

Figure 4.12 : The Oxidation by Chlorate of Tc^{IV} and Tc^{V} produced during the Tc-N_2H_4-$HClO_4$ Reaction

[Tc]	:	1.6×10^{-3} mol dm^{-3}
$[N_2H_4]$	:	0.1 mol dm^{-3}
$[HClO_4]$	:	2.0 mol dm^{-3}
$[NaClO_4]$	:	4.9 mol dm^{-3}
$[KClO_3]$	:	0.01 mol dm^{-3}
Temp	:	35°C


30
20
10
0
% Tc as Tc(IV) or Tc(V)
CHLORATE
ADDED
Tc(IV)
Tc(V)
45
65
85
105
125
145
165
TIME / Minutes

and the effects on these species of adding the chlorate ion. Both Tc^{IV} and Tc^{V} undergo rapid oxidation leaving only a small fraction of the initial concentration of each ion. Evidently the effect of adding chlorate ion is to terminate the hydrazine oxidation reactions rapidly by starving them of the required Tc^{V} and Tc^{VI}.

Using U.V.-visible spectroscopy it was confirmed that the reduced oxidation states of technetium, present as a result of the normal course of the Tc-hydrazine reaction in perchloric acid, are oxidised to pertechnetate ion by the chlorate ion. U.V.-visible spectra of chlorate-spiked samples, which initially showed a very strong absorbance below 200 nm due to the chlorate ion and a sharp peak around 262 nm due to the absorption of a Tc complex of unknown nature show that the species in solution underwent a fairly slow reaction over a period of 10-20 minutes. After this period the absorption peaks caused by the chlorate ion had decreased in intensity significantly and the sharp peak centred around 262 nm had been replaced by the two highly characteristic absorption peaks at 248 and 288 nm due to the pertechnetate ion.

As it was impossible to determine which Tc species was being oxidised in the complex Tc-N_2H_4 reaction mixtures, it was decided to prepare a solution containing the metal in only one oxidation state and to attempt to study its reaction rate. However, during the 15 second time lag between initiating the reaction and withdrawing the first aliquot for analysis, all the Tc^{V} had been oxidised. Thus the value of 82.7 $dm^3\ mol^{-1}\ s^{-1}$ obtained for the rate constant for the oxidation reaction between Tc^{V} and ClO_3^- is only approximate.

As a continuation of the investigation into the effects of chlorate ion on the reaction between Tc and hydrazine, a reaction mixture was prepared which contained TcO_4^- (1.6×10^{-3} mol dm^{-3}), N_2H_4 (0.1 mol

dm^{-3}) and $HClO_3$ (3.0 mol dm^{-3}). On initiating the reaction by adding the hydrazine solution, a white precipitate of unknown composition formed. At regular time intervals the solution was assayed for its Tc^{IV} and Tc^{V} content; none was detected in any sample. It can therefore be stated that the technetium-catalysed oxidation of hydrazine cannot take place in the presence of high concentrations of chlorate due to the extremely rapid reaction that occurs between ClO_3^- and Tc^{IV} or Tc^{V}.

4.5.2 The Addition of Hypochlorite Ion to Tc-N_2H_4 Solutions in Perchloric Acid

The effects of the addition of hypochlorite to the species present during the normal course of the Tc-N_2H_4 reaction in perchlorate media was investigated using U.V.-visible spectrophotometric techniques.

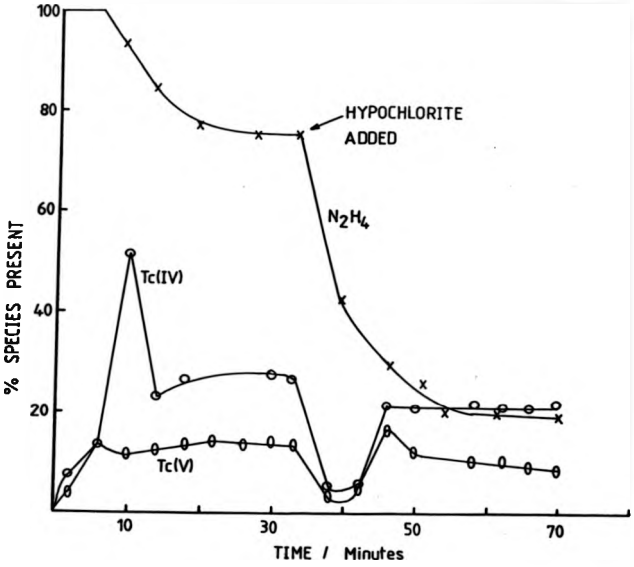
U.V.-visible spectra of the reaction mixture were recorded at regular time intervals while at the start of recording each spectrum an aliquot of the reaction mixture was withdrawn for colorimetric analysis for Tc^{IV} and Tc^{V} content. When the reaction had entered the fast reaction stage an aliquot of sodium hypochlorite ion solution was added. On addition of the hypochlorite ion, vigorous effervesence occurred with the evolution of chlorine gas, while the colour of the reaction changed from red-brown to an intense yellow (λ_{max} 344 nm).

The variation in the concentrations of Tc^{IV}, Tc^{V} and hydrazine with time are presented in Figure 4.13. It is clearly evident that the addition of hypochlorite causes a rapid oxidation of Tc^{IV}, Tc^{V} and hydrazine to occur, unlike chlorate ion which caused only the oxidation of Tc^{IV} and Tc^{V}.

An esr spectrum of the yellow reaction mixture was recorded at room

Figure 4.13 : The Effects of the Addition of Sodium Hypochlorite to a Tc-N_2H_4-$HClO_4$ Reaction Mixture during the Fast Reaction Stage.

[Tc]	:	1.6×10^{-3} mol dm^{-3}
[N_2H_4]	:	0.1 mol dm^{-3}
[$HClO_4$]	:	6.0 mol dm^{-3}
[$NaClO_4$]	:	0.9 mol dm^{-3}
[NaClO]	:	0.03 mol dm^{-3}
Temp	:	22°C


100
80
60
40
20
% SPECIES PRESENT
HYPOCHLORITE
ADDED
N_2H_4
Tc(IV)
Tc(V)
10
30
50
70
TIME / Minutes

temperature and an intense four-line spectrum was obtained with a_{Cl} = 17.50 ± 0.20 G and g_o = 2.0099 ± 0.0003; this has been identified as that of chlorine dioxide. An investigation into the origin of the chlorine dioxide revealed that the hypochlorite solution was contaminated with chlorite ion; acidification of this solution caused the two anions to react, liberating ClO_2.

In order to establish whether the loss of hydrazine from the solution was caused by its oxidation by ClO_2 or ClO^-, a fresh solution of hypochlorite was prepared by neutralising sodium hydroxide with chlorine gas. The results of this study showed that the oxidation of hydrazine by ClO^- is inhibited by acid; the reaction rate in an unacidified solution being 1.6 x 10^{-4} mol dm^{-3} s^{-1} while in 6 mol dm^{-3} $HClO_4$ the rate was 8.2 x 10^{-5} mol dm^{-3} s^{-1} (at 26°C).

Therefore the loss of hydrazine from the solution will be due partly to its oxidation by ClO^- and also partly due to reaction with ClO_2. On complete reaction of these two species, sufficient hydrazine remains in the solution to allow the reaction between Tc-H_2H_4 and $HClO_4$ to continue as normal.

4.6 The Formation of Coloured Complexes during the Tc-H_2H_4 Reaction in Perchloric Acid

As already stated in Section 4.1, the reduction of TcO_4^- ion by hydrazine leads to the production of large amounts of hydrated technetium dioxide. However, this compound is formed only at low perchlorate ion concentrations (1 mol dm^{-3}), at higher perchlorate ion concentrations the oxide does not precipitate and the Tc^{IV} remains in solution. Sundrehagen (121) has published several U.V.-visible spectra of $TcO(OH)_2$ and its polymerisation products in perchloric acid. The $TcO(OH)_2$ complex displays an absorbance

increasing from 300 nm to 197 nm with maxima at 275, 243, 212 and 197 nm.

The U.V.-visible spectra we have recorded of solutions resulting from the reduction of the pertechnetate ion by hydrazine in $HClO_4$ media show a strong absorbance around 190 nm with a shoulder at 212 nm and it is proposed that the latter peak is due to the $TcO(OH)_2$ complex, whilst the former is due to both the chlorate ion and $TcO(OH)_2$. The shoulders in the absorption spectrum at 275 and 243 nm are not visible as they are masked by the peaks at 248 nm and 288 nm due to the TcO_4^- ion. Jowtscheff et al. (122), who also published an absorption spectrum of $TcO(OH)_2$, show that the complex absorbs light up to 350 nm.

For concentrations of perchloric acid greater than 1 mol dm^{-3}, the reaction mixtures, which are all initially a pale yellow colour, become dark yellow-brown during the fast reaction stage, the colouration becoming more intense with increasing acidity. This dark brown colouration, presumably due to a Tc^{IV} complex, persists for several days. In 1 - 2 mol dm^{-3} acid, however, the solutions become a pale red colour after 24 hours, and at 6 mol dm^{-3} acid, after 5 - 6 days the solutions become an intense yellow colour due to the formation of the Tc^{VI} complex, $TcNCl_5^{2-}$.

In order to determine the nature of the complexes produced during the reaction, esr spectra of both room temperature solutions and frozen glasses were recorded.

Spectra of the dark yellow-brown reaction mixture in 6 mol dm^{-3} perchloric acid were recorded. At 77 K a 10-line Tc-centred esr spectrum was recorded; analysis of this spectrum has led us to believe it to be due to the Tc^{II} complex $Tc(NO)Cl_5^{2-}$. The esr parameters of this species together with literature values are

presented in Table 4.1.

The addition of ammonium thiocyanate to this solution, in an attempt to determine the amount of Tc^{IV} and Tc^{V} present, led to the immediate production of a dark, ink-blue complex, rather than the expected yellow or red colour. The esr spectrum of this blue complex, which was found to be completely extracted into *n*-butyl acetate, also showed 10-lines due to a Tc-centred species. The addition of thiocyanate ion led to a ligand exchange reaction to produce a complex similar to $[Tc(NO)NCS_5]^{2-}$; our values of A and g however differ slightly from those published for this complex. It is quite possible that we have produced a derivative of $[Tc(NO)(NCS)_5]^{2-}$ with several thiocyanate ligands being replaced by Cl^- or the solvent. Table 4.1 shows the esr parameters for our complex and those obtained from the literature.

As stated earlier, on standing for 5 - 6 days reaction mixtures in 6 mol dm^{-3} perchloric acid became an intense yellow (λ_{max} 398 nm these solutions also exhibited a 10-line Tc-centred spectrum (Figure 4.14) due unexpectedly to the Tc^{VI} complex, $[TcNCl_5]^{2-}$ (see Table 4.1 for esr parameters). Confirmation of the presence of this species comes from its U.V.-visible spectrum, which displays a λ_{max} value of 398 nm in agreement with that published by Baldas et al. (123).

The addition of ammonium thiocyanate to this solution also led to the production of an ink-blue complex which displayed the same 10-line spectrum at 77 K as that for $[Tc(NO)(SCN)_5]^{2-}$ with identical spectral parameters.

For reactions carried out in the lower acidity range of 1 - 2 mol dm^{-3}, the formation of a red complex in the solution was observed. This complex was clearly diamagnetic as no esr spectrum was

Table 4.1: : E.S.R. Spectral Parameters of Tc-centred Complexes Produced during the Tc-Hydrazine Reaction in $HClO_4$, together with Published Values for these Species

Complex	g_{11}	$g_{\perp}$	g_0	A_{11} / G	$A_{\perp}$ / G	A_0 / G	Author
$[Tc(NO)(NCS)_5]^{2-}$	1.936	2.042	2.007	266	104	158	Kirmse (126)
$[Tc(NO)(NCS)_5]^{2-}$	1.928	2.045	2./006	262	100	154	Baldas (127)
$[Tc(NO)(NCS)_x]^{2-}$	1.940	1.998	1.980	288	132	184	*
$[Tc(NO)Cl_5]^{2-}$	1.985	2.037	1.020	281	117	172	Kirmse (126)
$[Tc(NO)Cl_5]^{2-}$				292	119	177	*
$[TcNCl_5]^{2-}$	2.016	2.003	2.007	313	145	201	Kirmse (128)
$[TcNCl_5]^{2-}$	1.966	1.993	1.984	326	145	205	*
$[TcNCl_5]^{2-}$	1.969	1.992	1.984	326	145	205	+

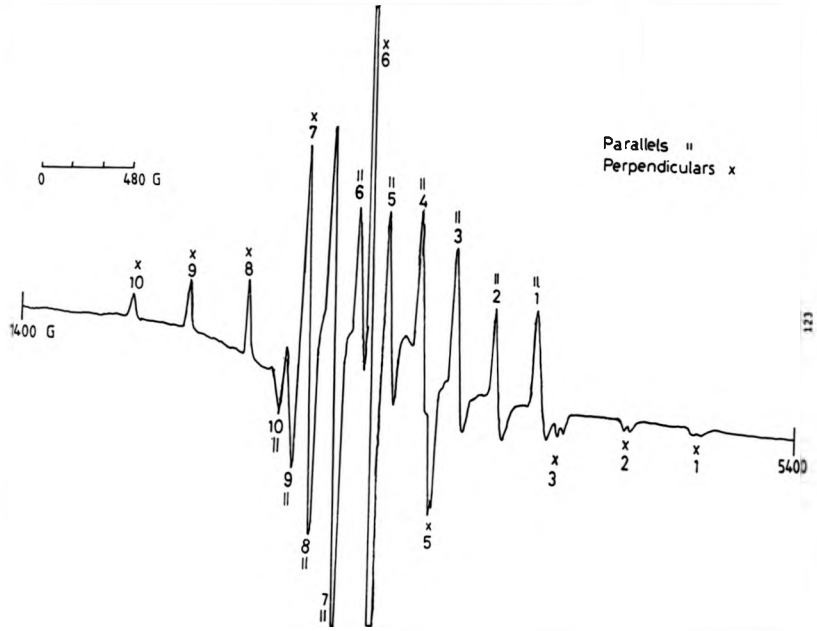
* Our experimental data from Tc-N_2H_4 systems

+ Prepared by the reaction between $[TcOCl_5]^{2-}$ and NaN_3

Figure 4.14 : The E.S.R. Spectrum of $TcNCl_5^{2-}$ formed on standing for several Days in a 6 mol dm^{-3} Perchloric Acid Reaction Mixture

Initial Reaction Conditions

[Tc]	:	1.6 x 10^{-3} mol dm^{-3}
$[N_2H_4]$	:	0.1 mol dm^{-3}
$[HClO_4]$	:	6.0 mol dm^{-3}
$[NaClO_4]$	:	0.9 mol dm^{-3}


Parallels ||
Perpendiculars x
0
480 G
1400 G
5400
x 10
x 9
x 8
x 7
|| 6
x 6
|| 5
|| 4
|| 3
|| 2
|| 1
10 ||
9 ||
8 ||
7 ||
x 5
x 3
x 2
x 1

obtained at either 298 or 77 K. It is possible that this pink complex could be a derivative of the yellow Tc^{VI} nitrido species Baldas et al. (123) observed that solutions of $Cs_2[TcNCl_5]$ in 5.6 mol dm^{-3} HCl contained $TcNCl_5^{2-}$ as the only Tc species. Dilution to 0.5 mol dm^{-3} acid however resulted in the formation of a pink diamagnetic species (λ_{max} 540 nm). We recorded several U.V.-visible spectra of the pink reaction mixtures obtained in 1 - 2 mol dm^{-3} $HClO_4$ and obtained values of λ_{max} from 530 to 550 nm, some variation being observed depending on the acidity and age of the solution. It is therefore proposed that the pink complex present in these solutions may well be that described by Baldas et al., i.e. $TcN(OH)_3$ or a polymeric hydrate form with -TcN-O-TcN- bridges such as $[TcN(\mu\text{-}O)(OH)H_2O]_n$ (123).

The presence of technetium nitroso complexes was quite unexpected as we did not consider it likely that hydrazine would be oxidised to produce nitric oxide even in small quantities. This assumption however proved to be incorrect as apart from detecting nitroso complexes, g.c.-m.s. analysis of samples of the gases evolved during the rapid oxidation stage of hydrazine indicated the presence of nitric oxide and NO_2, the latter being produced probably by reaction of nitric oxide with dioxygen.

This discovery of the production of NO during the oxidation of hydrazine led us to investigate further the effects of NO on the intermediate Tc species produced during the Tc-hydrazine reaction. Nitric oxide was generated by the reaction between KBr (8.5 g), $NaNO_2$ (4.5 g) and $FeSO_4 \cdot 7H_2O$ (8.5 g); on mixing, the solids react to liberate about 1 dm^3 of NO gas of composition 98.8% NO and 1.2% N_2 (124).

After initiating the Tc-hydrazine reaction, the apparatus was purged

with nitrogen to remove the air from the system to prevent the formation of nitrogen dioxide. When NO was passed through a pertechnetate solution, or a Tc-N_2H_4 reaction mixture which was still in the initiation stage, no colour change of the solution was observed. If, however, the gas was bubbled through a solution which had entered the fast reaction stage and therefore contained large amounts of reduced technetium, a rapid colour change from yellow or yellow-brown to a deep red occurred. The addition of nitric oxide appears therefore to have caused both the reduction of the technetium below the usual oxidation state of four and also the complexation of the reduction products. However if NO is passed through a solution in which a substantial portion of the technetium is present as the precipitated dioxide, then no colour change occurs and the supernatant liquid remains a a clear yellow colour. We propose that during the latter stages of the Tc-hydrazine reaction, when some of the perchlorate has been reduced to chloride, that some of the Tc^{IV} will be present as $[TcCl_6]^{2-}$ or its hydrolysis products and that Tc^{V} will probably be present to some extent as the $[TcOCl_4]^{-}$ ion.

It was shown by Orvig (125) that heating TcO_2 . x H_2O in HCl in a stream of NO gas gives mostly $[TcCl_6]^{2-}$, with only traces of $[Tc(NO)Cl_5]^{2-}$ being produced, therefore at our experimental temperature of 35°C it is probable that no reaction would occur. Orvig also showed that the reaction of $[TcOCl_4]^{-}$ with NO gas also caused the formation of $[TcCl_6]^{2-}$, with no evidence of further reduction to a Tc^{II} species.

The absence of any paramagnetic species in solutions treated with NO which contained TcO_2 in $HClO_4$ can therefore be explained as due to the TcO_2, Tc^{IV} or Tc^{V} chloro complexes proving resistant to

reduction by nitric oxide.

However, the treatment of reaction mixtures in 6 mol dm^{-3} $HClO_4$ which have just entered the fast reaction stage of hydrazine oxidation resulted in the formation of deep red solutions with λ_{max} values varying from 490 - 530 nm showing that a range of complexes was being produced. Analysis of these solutions using esr spectroscopy proved difficult as some samples contained paramagnetic species and others did not ; no correlation could be found between a particular λ_{max} value and the presence of a paramagnetic Tc^{II} nitrosyl complex. Those solutions which did give an esr spectrum contained two or more paramagnetic complexes leading to complex spectra as in Figure 4.15; the main component of this spectrum is due to the $[Tc(NO)Cl_5]^{2-}$ ion.

Conclusions

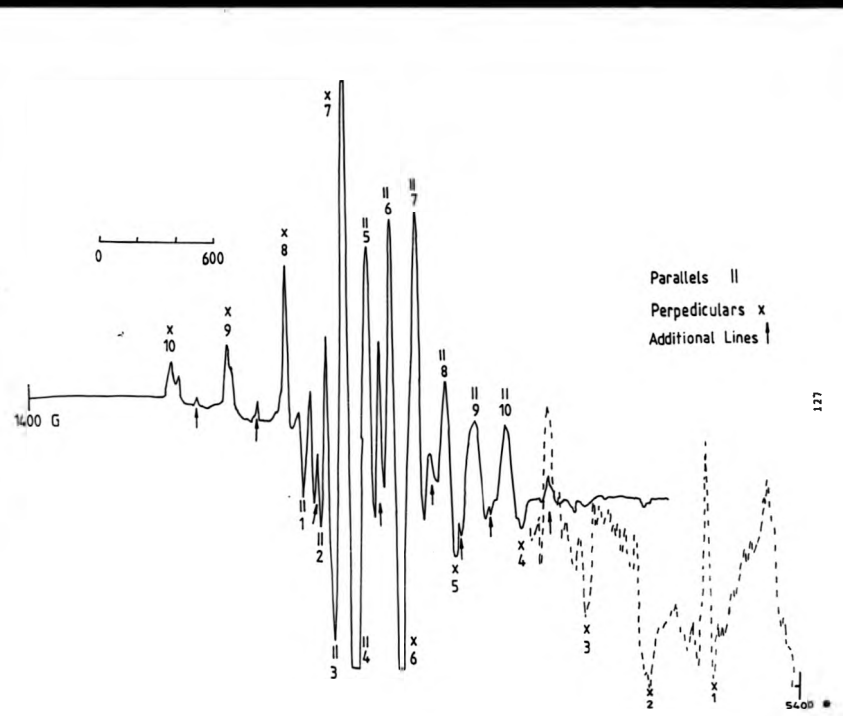
The yellow colouration that arises during the early stages of the reaction between TcO_4^- and hydrazine is due to the formation of hydrolysis products of technetium dioxide for instance, $TcO(OH)_2$. The appearance in the later stages of the reaction of a dense black precipitate is caused by the production of hydrated TcO_2.

As the Tc-hydrazine reaction proceeds, the perchlorate ion is reduced, eventually producing chloride ion. It is proposed that the chloride ion thus formed complexes with the technetium forming Tc^{V}, Tc^{IV}, Tc^{II} and possibly Tc^{I} complexes. The formation of Tc^{IV} chloro complexes will contribute to the yellow colour of the reaction mixtures.

The production of traces of nitric oxide as an oxidation product of hydrazine leads to the formation of trace quantities of the Tc^{II} complex $[Tc(NO)Cl_5]^{2-}$, presumably by reduction to Tc^{IV}. The addition of ammonium thiocyanate to these solutions produces an

Figure 4.15 : The E.S.R. Spectrum of a Dark Red Reaction Mixture produced by passing Nitric Oxide through a 6 mol dm^{-3} $HClO_4$ Reaction Mixture during the Fast Reaction Stage

[Tc]	:	1.6 x 10^{-3} mol dm^{-3}
$[N_2H_4]$	:	0.1 mol dm^{-3}
$[HClO_4]$	:	6.0 mol dm^{-3}
Temp	:	35°C
NO	:	1 dm^3


0
600
1400 G
Parallels II
Perpedicular x
Additional Lines
5400
127

ink-blue solution which displays an esr spectrum similar to that of $[Tc(NO)(NCS)_5]^{2-}$; these slight differences led us to suggest the possibility of the production of a complex in which one or more of the thiocyanate ligands has been replaced by a chloride ion or a solvent molecule (n-butyl acetate).

The effects of passing nitric oxide through Tc-hydrazine reaction mixtures during the fast reaction stage of hydrazine oxidation caused the formation of deep red solutions displaying λ_{max} values varying from 490 - 530nm. Some of these solutions contained the paramagnetic $[Tc(NO)Cl_5]^{2-}$ ion, but others displayed no esr spectrum either at 298 K or 77 K. It is suggested that the addition of large amounts of NO to the reaction mixtures may cause the reduction of the Tc^{II} nitrosyl complexes to Tc^{I}, resulting in the absence of paramagnetism.

As a result of the slow reaction between Tc^{V} or Tc^{IV} and the azide ion, low concentrations of the yellow technetium(VI) complex $[TcNCl_5]^{2-}$ develop; this is usually observed in the higher acidity (5-6 mol dm^{-3}) perchloric acid systems. Esr spectra of these solutions display 10 lines due to the presence of the nitrido complex; however, if aged (1-2 days) solutions are used, the main component in the solution is the $[Tc(NO)Cl_5]^{2-}$ ion, the additional lines in its esr spectrum probably being caused by traces of the yellow Tc^{VI} nitride.

4.7 Computer Simulation of the Tc-Hydrazine Reaction in a Perchloric Acid-Sodium Perchlorate System

The reaction was simulated, as with the nitric acid system, using software originally produced by P. D. Wilson; the equation sets and rate constants employed however are wholly new as the

simulation suite was originally composed for use with a nitrate-containing system.

Perchlorate systems display several features not found in nitrate media. Hydrazine destruction is complete and the production of Tc^{IV} is characterised by an initial peak at the onset of the fast reaction followed by a second peak during the fast reaction. In order to computer simulate this double wave the production of an intermediate Tc^{III} state is found to be necessary. The basic reaction scheme and the individual rate constants used in our simulation are presented in Table 4.2. (Tc^{III} is a component of the reaction scheme proposed by Zalvarte (2) for the Tc-hydrazine system).

The simulation of the reaction in perchlorate media transpired to be a very complex process. Apart from postulating the production of an intermediate Tc^{III} species, it was found necessary to invoke the production of three different intermediate Tc^{IV} complexes formed at different stages of the reaction. This production of Tc^{IV} complexes of differing reactivities is compatible with our earlier explanation of Tc-chloro or oxychloro complexes.

The situation is further complicated by the conversion of the perchlorate to chlorate, chlorite and hypochlorite ions, all of which will react with reduced oxidation states of technetium. Hypochlorite ion causes additional problems in that is oxidises hydrazine. However, in order to simplify the simulation, those reactions involving oxychloro ions other than perchlorate have been omitted.

It proved possible to reliably simulate the correct rate of oxidation of hydrazine during both the fast reaction stage and the termination stages. Unfortunately, we have not been able to

Table 4.2 : Equations and Rate Constants used in the Computer Simulation of the Tc-Hydrazine Reaction in Perchloric Acid

				Rate Constant / $dm^3\ mol^{-1}\ s^{-1}$
1	$Tc(VII) + N_2H_4$	⟶	$Tc(VI) + N_2H_{4(ox)}$	0.083
2	$Tc(VI) + H^+$	⟶	$Tc(VI)H$	5.6×10^{-3}
3	$Tc(VI)H + N_2H_4 + H^+$	⟶	$Tc(IV)_a + N_2H_{4(ox)}$	0.241
4	$Tc(VII) + Tc(IV)_a$	⟶	$Tc(VI)H + Tc(V)$	5.556
5	$Tc(V) + N_2H_4 + H^+$	⟶	$Tc(III) + N_2H_{4(ox)}$	10.00
6	$Tc(IV)_a + ClO_4^- + H^+$	⟶	$Tc(VI)H + ClO_3^-$	1.7×10^{-3}
7	$Tc(III) + ClO_4^-$	⟶	$Tc(V) + ClO_3^-$	1.1×10^{-3}
8	$Tc(V) + ClO_4^-$	⟶	$Tc(VI) + ClO_4^{-\cdot}$	0.10
9	$Tc(V) + ClO_4^-$	⟶	$Tc(VII) + ClO_3^-$	2.8×10^{-3}
10	$Tc(III) + ClO_4^- + H^+$	⟶	$Tc(IV)_b + ClO_4^{-\cdot}$	1.7×10^{-5}
11	$Tc(IV)_a + ClO_4^-$	⟶	$Tc(V) + ClO_3^-$	1.7×10^{-4}
12	$Tc(VI)H + ClO_4^-$	⟶	$Tc(VII) + ClO_3^-$	2.2×10^{-3}
13	$Tc(IV)_b + ClO_4^- + H^+$	⟶	$Tc(VI)H + ClO_3^-$	8.3×10^{-7}
14	$Tc(III) + ClO_4^- + H^+$	⟶	$Tc(IV)_c$	1.4×10^{-6}

where : $N_2H_{4(ox)}$ is an oxidation product of hydrazine; $Tc(IV)_a$, $Tc(IV)_b$ and $Tc(IV)_c$ are different complexes of Tc(IV)

reproduce the correct length of the initiation period except at elevated acidities (5-6 mol dm^{-3}). Typical results of simulating the time-profiles of hydrazine and Tc^{IV} concentrations for two acidities are presented in Figure 4.16.

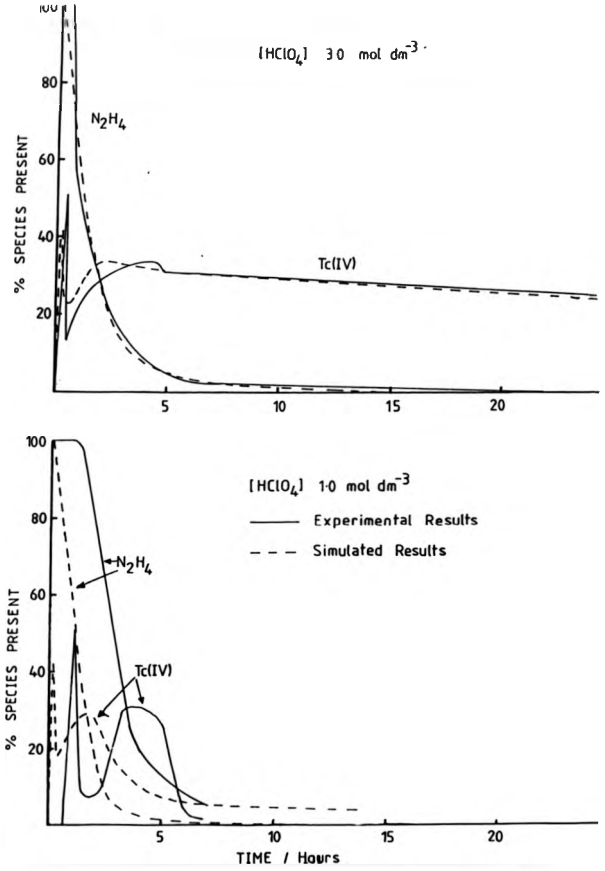
From this figure it can also be seen that we have reproduced adequately the peculiar features in the changing concentrations of Tc^{IV} in the system. In order to simulate the sharp spike in the concentration of Tc^{IV} at the onset of the reaction, it was found necessary to increase the rate at which pertechnetate reacted with hydrazine (thus causing the loss of the initiation stage in the simulation).

As the acidity of the reaction mixtures was raised, it was found that a closer fit to the experimental data was obtained, as illustrated in Figure 4.16.

As with the simulation of the reaction in nitrate-containing media, it is accepted that the so-called rate constants are not true constants, but instead "best-fit" rate constants which provide an adequate match to the experimental data, i.e. they probably include contributions from several additional minor reactions.

Figure 4.16 : Computer Simulation of the Changing Concentration Profiles of Hydrazine and Tc^{IV} during the Tc-N_2H_4 Reaction in 1.0 and 3.0 mol dm^{-3} Perchloric Acid

[Tc]	:	1.6 x 10^{-3} mol dm^{-3}
[N_2H_4]	:	0.1 mol dm^{-3}
[$HClO_4$]	:	1.0 or 3.0 mol dm^{-3}
[$NaClO_4$]	:	5.9 or 3.9 mol dm^{-3}
Temp	:	35°C


[HClO4] 3·0 mol dm-3
N2H4
Tc(IV)
% SPECIES PRESENT
100
80
60
40
20
5
10
15
20
[HClO4] 1·0 mol dm-3
Experimental Results
Simulated Results
N2H4
Tc(IV)
% SPECIES PRESENT
TIME / Hours

4.8 Discussion

As already mentioned, the reaction scheme that takes place in perchlorate media appears to be far more complex than that which occurs in nitric acid.

The profile of hydrazine oxidation typically displays an induction period and a fast reaction stage leading to the complete destruction of the hydrazine. The acidity dependence of this reaction has been shown to be opposite to that for the reaction in nitric acid, i.e., increasing acidities shorten, rather than lengthen the initiation stage and also increase the rate of the fast reaction.

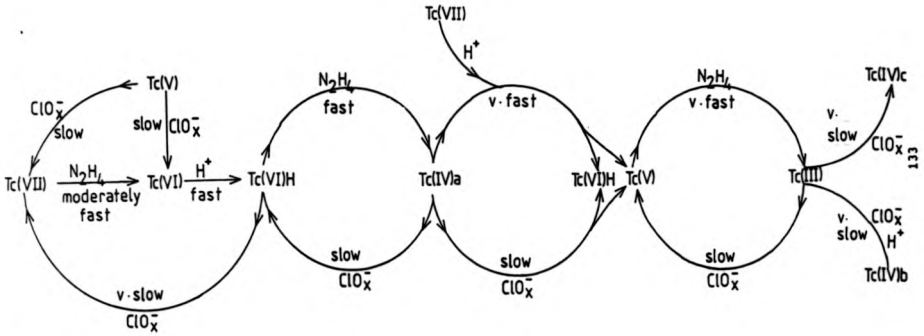
The postulated reaction scheme for the perchlorate system which is used in the computer simulation is presented in Figure 4.17. We propose that TcO_4^- undergoes a moderately fast reaction with hydrazine to give technetate ion which is then protonated by perchloric acid. This step is absent in nitric acid as HNO_3 does not have a sufficiently high dissociation constant to effect protonation of the TcO_4^{2-} ion. The protonated Tc^{VI} then reacts with hydrazine, undergoing a 2-electron reduction to Tc^{IV}. It is considered that the Tc^{IV} species produced at this early stage of the reaction is probably $[TcO(OH)_2]$, with $TcO_2.xH_2O$ being produced at low (1.0 mol dm^{-3}) perchlorate ion concentrations.

From our study of the U.V.-visible spectral changes, we believe the fast reaction stage commences when approximately 50% of the TcO_4^- has been reduced to Tc^{IV}.

The early stages of the fast reaction involve two reactions: the comproportionation reaction between TcO_4^- and Tc^{IV} to give Tc^{VI} and Tc^{V} and the 2-electron oxidation of hydrazine by Tc^{VI} to give Tc^{IV} and also the oxidation of hydrazine by Tc^{V} to Tc^{III}.

The production of Tc^{III} at this stage was postulated as it enables

Figure 4.17 : The Proposed Reaction Scheme for the Reaction between TcO_4^- and Hydrazine in Perchloric Acid.



ClO_x^- : Where x = 1.- 4

simulation of the production of a sharp peak in the concentration of Tc^{IV} prior to the fast reaction commencing, and also the formation of a broad peak in Tc^{IV} concentration once the fast reaction has started. The eventual fate of the Tc^{III} is to be oxidised by one of the oxochloro ions in solution to either Tc^{V}, or one of two Tc^{IV} complexes. The rate of production of these Tc^{IV} complexes is acid-dependant and enables the residual concentration of Tc^{IV} remaining after termination of the reaction to the simulated. It will be remembered from earlier sections that the yield of Tc^{IV} after the complete loss of hydrazine from the solution is acid-dependant and varies from 10% in 1 mol dm^{-3} $HClO_4$ to 25% in 6 mol dm^{-3} acid.

The termination reaction is the very slow oxidation of the protonated form of Tc^{VI} to TcO_4^-; this reaction, like all other oxidation steps of Tc in the system could be by any of the range of oxychloro ions present as a result of the reduction of perchlorate.

We have determined the rates of oxidation of Tc^{IV} and Tc^{V} by chlorate and have obtained values of 3.1 dm^3 mol^{-1} s^{-1} and 82.7 dm^3 mol^{-1} s^{-1} respectively at 35°C. It can therefore be stated that the oxidation steps of reduced Tc species by chlorate are far more rapid than the identical reactions involving the less kinetically active perchlorate ion.

Due to the highly reactive nature of chlorate and presumably chlorite and hypochlorite ions in acid solutions, it is considered that the half-life of these ions will be short and therefore only low concentrations will be attained.

The amount of free chloride ions produced in a 2 mol dm^{-3} $HClO_4$ reaction mixture was determined 24 hours after initiation, using silver chloride gravimetric analysis. It was found that 3.2×10^{-2}

mol dm^{-3} of chloride were present. Thus the oxidation of 0.1 mol dm^{-3} of hydrazine led to the production of 3.2×10^{-2} mol dm^{-3} of chloride ion. It is, however, probable that a slightly higher yield of chloride was produced but this was unavailable for precipitation with the silver due to prior complexation with technetium.

Assuming that hydrazine is oxidised via two 2-electron oxidation steps and that perchlorate is reduced via four 2-electron reduction steps, then 0.1 mol dm^{-3} of hydrazine would require 2 electron equivalents for complete oxidation, and the reduction of 0.032 mol dm^{-3} of perchlorate to Cl^- provides 1.28 electron equivalents. It can therefore be assumed that a substantial amount of the technetium in the solution is recycled via the Tc^{IV}, Tc^{VII} comproportionation reaction and also that finite amounts of chlorate, chlorite and hypochlorite ions exist in the solution.

The activation energy for the rate-determining step for the oxidation of hydrazine has been determined as 35.5 ± 1 kJ mol^{-1}. It is considered likely that this limiting step is analogous to the situation that occurs in nitric acid media, i.e. it is proposed that the slow step is the oxidation of Tc^{IV} to Tc^{VI} by perchlorate.

The activation energy of the rate determining step of the reaction leading to the production of ammonium ions was also determined and found to be 83 ± 12 kJ mol^{-1}. Unfortunately, problems with the reproducibility of the ammonium ion assay led to a greater error in the calculated rates of the fast reaction stage and hence the activation energy. The nature of the slow step with production of ammonium ion remains unknown.

4.9 Conclusions

The technetium-catalysed oxidation of hydrazine which occurs in perchlorate media is a complex process, which involves not only oxidation of technetium in lower oxidation states (and in several complexes) by perchlorate ion itself, but also by a whole family of oxy-chloro ions from chlorate to hypochlorite. The presence of ClO_2^- and ClO^- in the solution will lead to the production of trace concentrations of ClO_2, which reacts both with technetium and hydrazine.

It is proposed that the Tc^{VI} produced in the reaction is rapidly protonated by the strongly acidic perchloric acid medium and that this species may be more resistant to oxidation, partly explaining the absence of a termination step.

It has been shown that as the acidity is increased, the rates of the initiation reaction and fast reaction stages increase; this contrasts with the situation found in nitric acid where increased acidity leads to lengthening of the initiation period and eventually complete inhibition of hydrazine oxidation.

The oxidation of technetium by perchlorate leads to formation of low concentrations of chloride ions which form complexes with the technetium. It is proposed that the Tc^{IV} chloro or oxychloro complexes produced during the fast reaction stage are less susceptible to oxidation by perchlorate than the simple oxo complexes, thus explaining the appearance of a 10 - 25% yield of Tc^{IV} after complete loss of hydrazine from the solution.

The use of esr spectroscopy has shown that trace concentrations of the Tc^{II} complex $[Tc(NO)Cl_5]^{2-}$ are produced during the normal course of the Tc-hydrazine reaction and that after prolonged standing for several days the Tc^{VI} nitrido complex $[TcNCl_5]^{2-}$ is formed. The

addition of nitric oxide to the reaction mixtures results in the formation of deep red solutions which may contain diamagnetic Tc^{I} nitrosyl complexes.

5 A Study of the Reaction Kinetics and Intermediate Species produced during the Tc-Hydrazine Reaction in the Presence of a Variety of Acids.

5.1 An Investigation into the Reaction Kinetics of the Tc-Hydrazine Reaction in Trifluoroacetic Acid

In order to establish more precisely the effects of acidity on the rate of reaction between Tc and hydrazine, experiments were carried out in which the oxidising nitric or perchloric acids were replaced by trifluoroacetic acid. The reaction was studied at two acid concentrations; 1.0 and 4.7 mol dm^{-3}. It should be noted that these systems contained technetium as the only oxidant and hence the reactions observed will be those between technetium and hydrazine or its degradation products. The re-oxidation steps of reduced technetium by nitrate or perchlorate ions, the key feature of much of this thesis, will not occur.

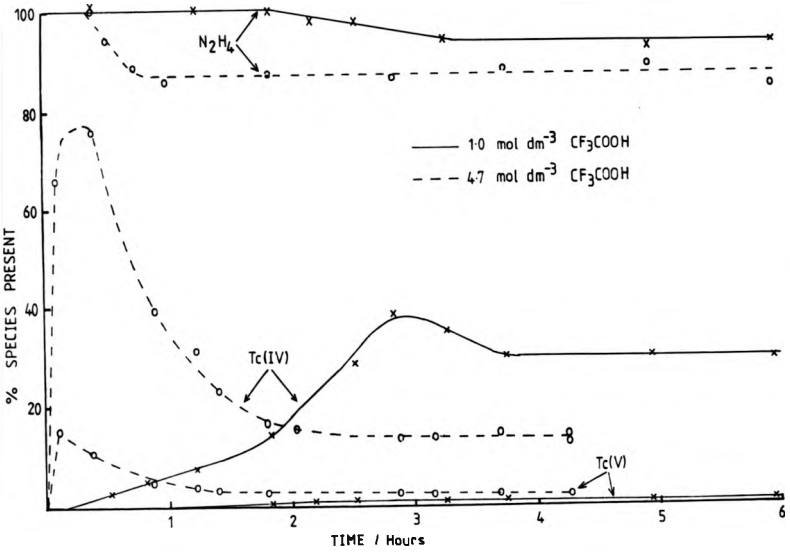
The solutions were assayed for their hydrazine, ammonium ion, Tc^{IV} and Tc^{V} contents. The results for the ammonium ion assay show yields of 1 x 10^{-3} mol dm^{-3}, or 15% at the higher acidity. Unfortunately, little credence can be placed on these results as such a low concentration is barely within the analytical limits of the assay. For the lower acid concentration of 1.0 mol dm^{-3}, the concentration of ammonium ion produced was so low that it did not exceed the limits of experimental error.

The changes of concentration of hydrazine, Tc^{IV} and Tc^{V} with time for both acidities studied are shown in Figure 5.1.

Considerable difficulties were experienced with the assays for Tc^{IV} and Tc^{V} , after the reaction had proceeded for approximately three hours, rather than obtaining a yellow aqueous phase and a red

Figure 5.1 : The Time-Profiles of the Concentrations of Hydrazine, Tc^{IV} and Tc^{V} at two Trifluoroacetic Acid Concentrations

[Tc]	:	1.6×10^{-3} mol dm^{-3}
$[N_2H_4]$	:	0.13 mol dm^{-3}
$[CF_3COOH]$	:	1.0 or 4.7 mol dm^{-3}
Temp	:	$35^{o}C$


100
80
60
40
20
% SPECIES PRESENT
N_2H_4
1·0 mol dm^{-3} CF_3COOH
4·7 mol dm^{-3} CF_3COOH
Tc(IV)
Tc(V)
1
2
3
4
5
6
TIME / Hours

n-butyl acetate phase as normally used to determine the concentrations of Tc^{IV} and Tc^{V} respectively, we obtained red aqueous and organic phases. In order to establish the effects of trifluoroacetic acid on the assay, increasing amounts of the acid were added to samples withdrawn from a $Tc-N_2H_4-HClO_4$ reaction mixture.On adding thiocyanate it was found that the λ_{max} values of the red and yellow complexes altered with increasing acidity, leading eventually to the production of both red aqueous and organic phases. It was found that there was some time-dependence as regards this interference, with samples withdrawn later in the reaction for Tc analysis being more susceptible to interference.

However, it can be assumed that the results shown in Figure 5.1 are relatively free from interference at least as regards three hours after initiation. It is clearly obvious from these results that the rate of hydrazine oxidation, and hence pertechnetate reduction, is greatly increased as the acidity is increased.

It would be expected that all the pertechnetate would be reduced to Tc^{IV}; this however proves not to be the case, and instead the yield of Tc^{IV} is found to be acid-dependent, as is the oxidation step when it is converted presumably back to TcO_4^-. It is expected that the step that leads to the removal of Tc^{IV} from the system is the comproportionation reaction between Tc^{IV} and TcO_4^- proposed by Garraway and Wilson (27).

A series of U.V.-visible spectra were recorded at three-minute time intervals during the course of a reaction carried out in 4.7 mol dm^{-3} trifluoroacetic acid. These spectra feature a decreasing absorbance due to the TcO_4^- ion, together with the appearance of a peak at 325 nm with a shoulder at 420 nm. An isosbestic point is found at 300 nm, showing that the solution contains two main

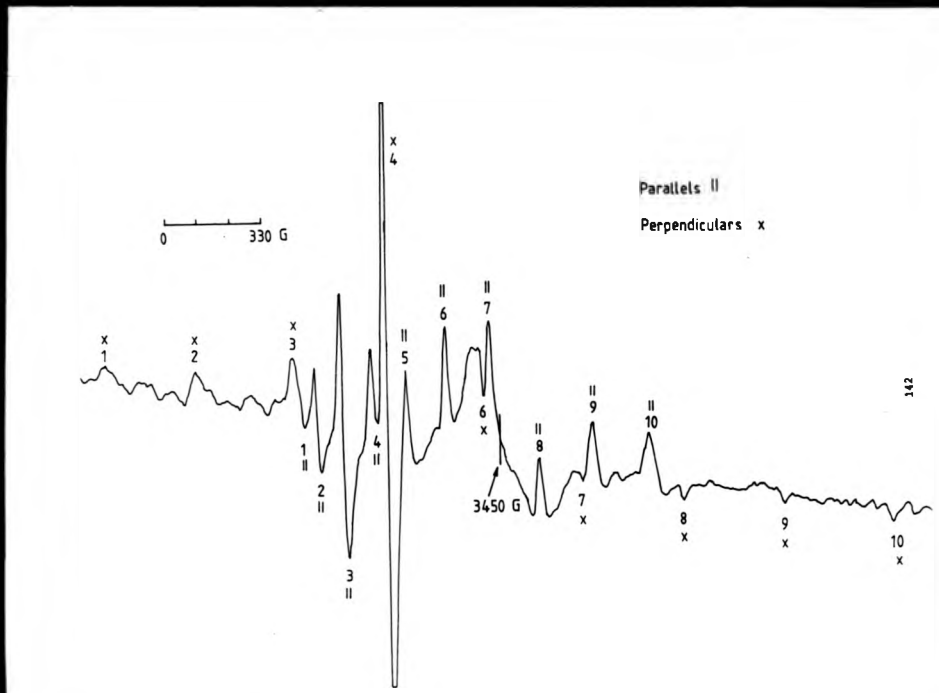
species, i.e. TcO_4^- and a second Tc species, presumably Tc^{IV}.

A plot of the absorbance at 246 nm (due to the TcO_4^- ion) versus that at 325 nm is linear, confirming that the pertechnetate is very rapidly converted to a species which absorbs light at 325 nm. After several hours the peaks due to the pertechnetate ion disappear and are replaced by a sharp peak at 216 nm. The peak at 325 nm is also found in HNO_3 media, showing that these systems contain a common Tc^{IV} complex.

An experiment was carried out in order to see whether the addition of nitric oxide to this system would produce paramagnetic complexes as was the case with all the systems previously examined. On passing NO through the solution the sharp peak at 216 nm was replaced by the two peaks due to the TcO_4^- ion, and a third peak was also observed to have appeared at 486 nm. Esr spectra of this solution were recorded at 298 and 77 K, no isotropic spectrum was observed but that recorded at 77 K appears to be completely new and does not appear in the literature (Figure 5.2). A tensors were calculated for this species and found to be $A_{||}$ 309 G, $A_{\perp}$135 G and A_0 193 G, which leads us to suggest that we have prepared a Tc^{II} nitrosyl complex with one or more trifluoroacetate ligands coordinating about the Tc centre.

Figure 5.2 : The E.S.R. Spectrum of the Tc^{II} Nitrosyl Complex formed by passing Nitric Oxide through a Tc-N_2H_4-Trifluoroacetic Acid Reaction Mixture

[Tc]	:	1.6×10^{-3} mol dm^{-3}
[N_2H_4]	:	0.1 mol dm^{-3}
[CF_3COOH]	:	1.0 mol dm^{-3}
Temp	:	$35^{o}C$
NO	:	1 dm^3


Parallels ||
Perpendiculars x
0
330 G
3450 G
142

5.2 An Investigation into the Reaction Kinetics of the Tc-Hydrazine Reaction in Tetrafluoroboric Acid

Due to the problems encountered in the assay for Tc^{IV} and Tc^{V} in the trifluoroacetic acid sytem, it was decided to use tetrafluoroboric acid in its place as experience showed that this acid did not interfere with the thiocyanate assay. We therefore concentrated attention on a study on the kinetics of the TcO_4^--hydrazine reaction in HBF_4.

The results obtained for the hydrazine oxidation profile and Tc^{IV} production are more compatible with what would be expected from the Garraway and Wilson model, than were the results from the trifluoroacetic acid system.

Two reaction mixtures were prepared in 0.5 and 3.0 mol dm^{-3} HBF_4, the ionic strength being maintained at μ = 5.7 mol dm^{-3} by adding sodium tetrafluoroborate. The solutions were assayed for their hydrazine, Tc^{IV} and Tc^{V} contents, and the results obtained are presented in Figure 5.3.

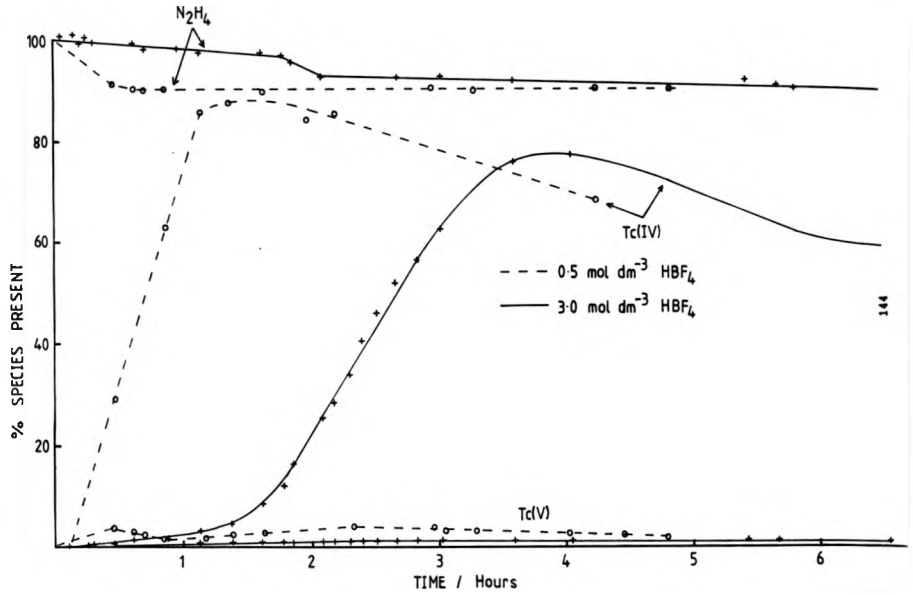
As in the case of the trifluoroacetic acid system, the reaction rate is increased as the acidity is increased, with both an increased rate of hydrazine oxidation during the fast reaction stage and a shortened initiation stage.

The yields of Tc^{IV} are far greater in this system and approach 90% in 3 mol dm^{-3} acid and 80% at the lower acidity. This is as expected from the Garraway and Wilson model (15) insofar as in the absence of an oxidant such as nitrate or perchlorate, the reduction of pertechnate should proceed until all the TcO_4^- had been reduced to Tc^{IV}.

After reaching a peak, the concentration of Tc^{IV} declines steadily for several hours and then enters a stage of very gradual decline

Figure 5.3 : The Time-Profiles of the Concentrations of Hydrazine, Tc^{IV} and Tc^{V} at two Tetrafluoroboric Acid Concentrations.

[Tc]	:	1.6×10^{-3} mol dm^{-3}
$[N_2H_4]$	:	0.1 mol dm^{-3}
$[HBF_4]$	:	0.5 or 3.0 mol dm^{-3}
$[NaBF_4]$	:	5.1 or 2.6 mol dm^{-3}
$[BF_4^-]_{Total}$	:	5.6 mol dm^{-3}
Temp	:	35°C


N_2H_4
100
80
60
40
20
% SPECIES PRESENT
Tc(IV)
0·5 mol dm^{-3} HBF_4
3·0 mol dm^{-3} HBF_4
144
Tc(V)
1
2
3
4
5
6
TIME / Hours

with the concentration falling from 60% at 7 hours to 20% after 24 hours in 0.5 mol dm^{-3} acid.

It is worth noting that at both acidities, in spite of the very high concentration of Tc^{IV} present, that no TcO_2 was precipitated from the solution, the reaction mixtures remaining a clear yellow/brown colour throughout. Clearly both in this system, and in trifluoroacetic acid media, the Tc^{IV} complexes produced are different from those found in the low ionic strength perchloric acid systems. This was also verified by the absence of any of the absorption peaks due to the $TcO(OH)_2$ complex thought to be present in the perchloric acid reaction mixtures.

As for the trifluoroacetic acid system, it is proposed that the decline in the concentration of Tc^{IV} after the end of the fast reaction stage is due to the comproportionation reaction between the Tc^{IV} and any unreduced TcO_4^- remaining in the solution. It is, however, unclear as to why the hydrazine oxidation reactions do not continue if the Tc^{IV} is being converted back to a form capable of reacting with hydrazine. It may be the case that the Tc^{VI} formed via the comproportionation reaction of Tc^{IV} and Tc^{VII} undergoes a rapid disproportionation reaction to give Tc^{VII} and Tc^{V}, thus terminating the reaction.

5.3 An Investigation into the Nature of the Tc^{IV} Complexes produced by the Reduction of TcO_4^- by Hydrazine in Hydrochloric Acid

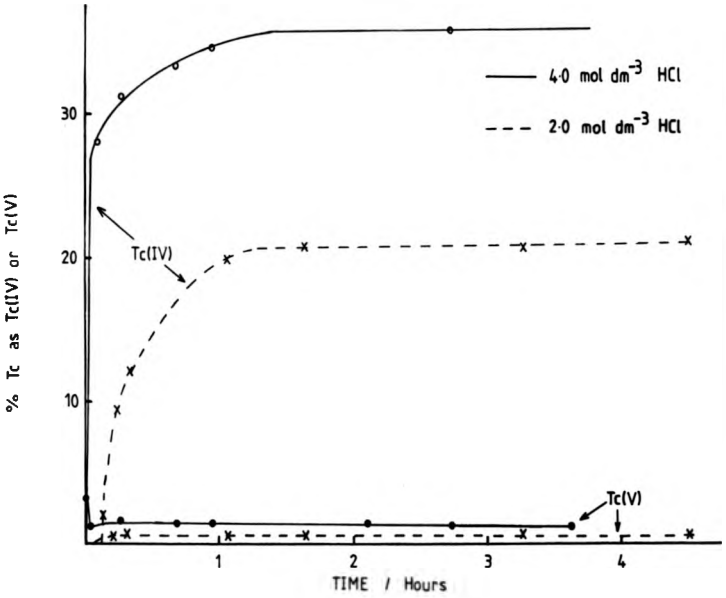
The reduction of pertechnetate ion by hydrazine in hydrochloric acid solutions of increasing acidity was followed using U.V.-visible spectroscopy and also by monitoring changes in the concentrations of Tc^{IV} and Tc^{V} using the thiocyanate colorimetric analysis. The solutions were also assayed for their hydrazine content, but due to the very low level of hydrazine conversion with resulting experimental scatter, these results are not included.

The reaction was followed spectrophotometrically in 4.0, 3.0 and 2.0 mol dm^{-3} HCl reaction mixtures. In 4.0 mol dm^{-3} hydrochloric acid the solution very rapidly became yellow and U.V.-visible spectra of the solution show peaks at 205, 241, 306 and 340 nm; these spectra are identical to those published for the $TcCl_6^{2-}$ ion. (129,130), although the presence of $[TcCl_5(H_2O)]^-$ cannot be ruled out due to an overlapping absorption spectrum (129). The results for the thiocyanate assay show that the concentration of Tc^{IV} reaches its peak level of 35% after 1.5 hours and thereafter remains constant. These results also show that a matter of seconds after initiating the reaction, the concentration of Tc^{V} has peaked at 3.3%, it then very rapidly declines and remains at approximately 1% for the remainder of the reaction. This production of a peak in the concentration of Tc^{V} almost instantaneously after initiating the reaction leads us to consider the possibilities (i) of a 2-electron reduction of TcO_4^- in the initiation reaction rather than a 1-electron reduction to Tc^{VI} or (ii) that in HCl the rate of the initiation stage is dramatically increased.

The results of the thiocyanate assay for the reaction in 4.0 and 2.0 mol dm^{-3} HCl are shown in Figure 5.4.

Figure 5.4 : Time-Profiles of the Concentrations of Tc^{IV} and Tc^{V} in Hydrochloric Acid Reaction Mixtures.

[Tc]	:	1.6×10^{-3} mol dm^{-3}
$[N_2H_4]$	:	0.1 mol dm^{-3}
[HCl]	:	2.0 or 4.0 mol dm^{-3}
Temp	:	$35^{o}c$


4·0 mol dm^{-3} HCl
2·0 mol dm^{-3} HCl
Tc(IV)
Tc(V)
% Tc as Tc(IV) or Tc(V)
TIME / Hours
10
20
30
1
2
3
4

It can be seen that the profile of Tc^{IV} evolution for a 2.0 mol dm^{-3} HCl reaction mixture closely parallels that of the higher acidity reaction mixture except that the yield of Tc^{IV} is approximately 40% lower.

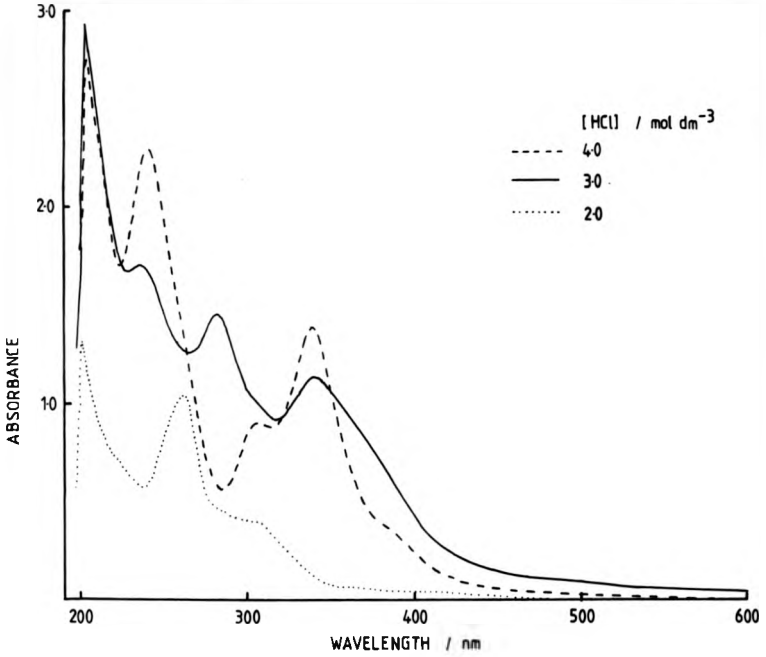
U.V.-visible spectra of reaction mixtures with acidities less than 4 mol dm^{-3} do not display the four absorption peaks due to the $TcCl_6^{2-}$ ion, but instead show different spectra due to the presence of hydrolysis products of $TcCl_6^{2-}$. These spectra are illustrated in Figure 5.5. It has not proved possible to identify any of the species present in the lower acidity reaction mixtures due to the complex nature of the spectra produced. Our study of publications on the aquation of the $TcCl_6^{2-}$ ion can however lead us to state that the complexes present in 3 - 2 mol dm^{-3} HCl are not $[TcCl_5(H_2O)]^-$ or $[TcCl_4(H_2O)_2]^{2-}$ but may instead be due to the presence of complexes with several chloride ligands replaced by water molecules. No evidence was found in any of the spectra recorded of the Tc^V species $[TcOCl_5]^{2-}$ which is not surprising in view of its reactivity towards hydrazine and the low concentration of Tc^V in the solutions. We have shown that the reaction between $[TcOCl_5]^{2-}$ and hydrazine in HCl (5.0 mol dm^{-3}) leads to the production of the same Tc^{IV} complex ($[TcCl_6]^{2-}$) as produced in the reaction between TcO_4^- and hydrazine in 4.0 mol dm^{-3} HCl. It is therefore considered likely that the Tc^V produced by the reduction of TcO_4^- will also be very rapidly complexed by chloride and will be present to some extent as $[TcOCl_5]^{2-}$.

5.4 Conclusion

The experimental results from these sections clearly show that in the absence of the oxidising mineral acids, HNO_3 or $HClO_4$,

Figure 5.5 : U.V.-visible Spectra of the Products of the Reaction between TcO_4^- and Hydrazine with varying Concentrations of Hydrochloric Acid

[Tc]	:	1.6×10^{-3} mol dm^{-3}
$[N_2H_4]$	:	0.1 mol dm^{-3}
[HCl]	:	Varied
Temp	:	25^oC


3·0
2·0
1·0
ABSORBANCE
200
300
400
500
600
WAVELENGTH / nm
[HCl] / mol dm^{-3}
4·0
3·0
2·0

technetium no longer functions as a catalyst towards the oxidation of hydrazine. The reaction proceeds until all the pertechnetate in the system has been reduced and then ceases; surprisingly only in HBF_4 media does the concentration of Tc^{IV} produce approximately 100%. The reasons for this are unclear as it would be expected that complete conversion of TcO_4^- to Tc^{IV} should occur in the presence of the non-oxidising acids studied.

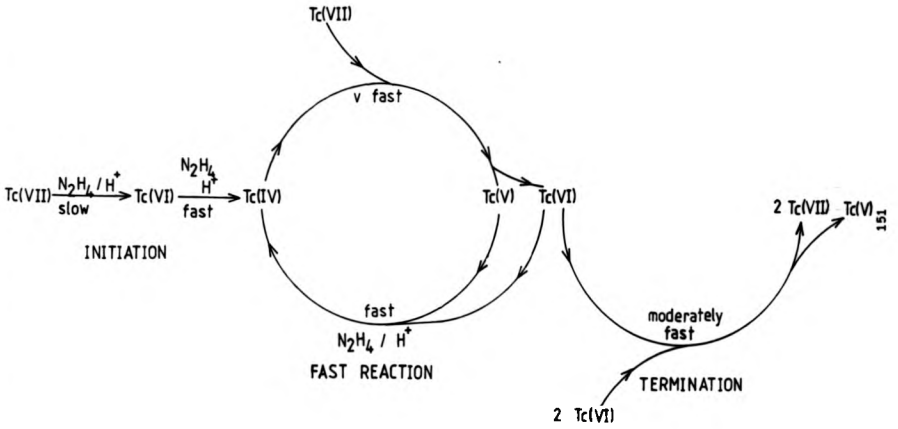
The time-profiles of the concentrations of Tc^{IV} in trifluoroacetic acid and HBF_4 media show that the production of Tc^{IV} reaches a peak and thereafter declines steadily; this reoxidation of Tc does not however lead to the further oxidation of hydrazine. It is also evident that the reaction displays a marked dependence towards acidity with the rates of the initiation and fast reaction stages being increased with increasing acidity. We propose the reaction scheme to account for these observations summarised in Figure 5.6.

The only major difference between this scheme and that proposed by Garraway and Wilson (15) for the reaction in nitric acid, apart from the obvious lack of oxidation steps of reduced technetium complexes to TcO_4^-, is the disproportionation of Tc^{VI}. It is proposed that the termination reaction involves two stages. In the first step Tc^{IV} and TcO_4^- undergo a comproportionation reaction to give Tc^{V} and Tc^{VI}. The Tc^{VI} produced then undergoes a disproportionation reaction to give Tc^{VII} and Tc^{V}, thus leading to the gradual removal of Tc^{IV} from the solutions.

It is expected that the concentration of Tc^{IV} in the hydrochloric acid reaction mixtures would undergo the same ultimate decrease in concentration; this was not observed however as the reaction was only followed for the first few hours.

We have shown that in hydrochloric acid media, the major reduction

Figure 5.6 : The Proposed Reaction Scheme for the Reduction of Pertechnetate by Hydrazine in the Absence of an Oxidising Mineral Acid


Tc(VII)
v fast
Tc(VII) N_2H_4 / H^+ slow Tc(VI) N_2H_4 H^+ fast Tc(IV)
Tc(V)
Tc(VI)
2 Tc(VII) Tc(V)
151
INITIATION
fast
N_2H_4 / H^+
FAST REACTION
moderately fast
TERMINATION
2 Tc(VI)

product of pertechnetate is the $TcCl_6^{2-}$ ion in 4 mol dm^{-3} HCl; for lower acid concentrations it is considered that aquation of this complex leads to the formation of a species with two or more chloride ligands replaced by water molecules. The U.V.-visible spectrum of the species produced in 2 mol dm^{-3} HCl is identical with that obtained by Garraway and Wilson (27) for a reduction product of TcO_4^- by hydrazine in a mixed HCl-HNO_3 solution, thus similarities exist between this system and that also containing HNO_3.

6.1 The Tc(V)-Azide Reaction

The reaction between the azide ion and Tc(V), present as $[TcOCl_4]^-$, in hydrochloric acid (7 - 11.6 mol dm^{-3}) was investigated in order to establish whether the destruction of azide in the Tc-N_2H_4 reaction is due to the reaction with azide and a metal ion or due to that between azide and $N_2H_4^+$ as proposed by Garraway and Wilson (39,40,128).

In recent years several papers have been published on the preparation and esr properties of Tc(VI) nitrido species (39,40,128), these complexes being of interest as they have similar biological distribution properties to Tc=O species with the same ligands. The nitrido ligand (N^{3-}) is isoelectronic with the oxo ligand (O^{2-}) and is a powerful π-electron donor which tends to stabilise metals in high oxidation states. Such an example is the $[TcNCl_5]^{2-}$ ion, due to the paramagnetism of Tc^{VI} complexes it proved possible to detect this complex at low concentration in solution using esr spectroscopy.

Experimental

The Tc(V) complex $[TcOCl_4]^-$ was prepared by adding ammonium pertechnetate to concentrated hydrochloric acid (11.6 mol dm^{-3}). The reaction is supposedly instantaneous, although it was found in practice that one or two hours were required for a reproducible and stable U.V.-visible spectrum to be obtained.

An aliquot of the aged Tc(V) stock solution was taken and the reaction initiated by adding an aliquot of the sodium azide solution. On addition of the azide the solution immediately began to develop a yellow colour.

The course of the reaction was monitored by recording U.V.-visible absorption spectra at regular time intervals and by

following the changing concentrations of Tc^{IV} and Tc^{V} in the solution using the thiocyanate colorimetric assay.

Figure 6.1 shows the changing absorption spectrum of the reaction mixture with time. As the Tc(V) is oxidised, the peak at 292 nm decreases in intensity; this is accompanied by an increase in absorbance at 399 nm.

The results of the thiocyanate assay for Tc(V) and (IV) cannot be used during the first half of the reaction because of the incomplete extraction of the red thiocyanate complex and subsequent interference with the Tc(IV) assay. The results obtained for the later stage of the reaction seem reliable; at 32 minutes 2% of the technetium was present as Tc(IV) and 4% as Tc(V). Thus 94% of the metal had been oxidised to $[TcNCl_5]^{2-}$.

The rate of production of Tc^{VI}, for two different azide concentrations was followed by monitoring the increasing absorbance at 399 nm; as expected the results for the lower concentration of azide show a more marked inhibition in the reaction rate as the Tc^{V} concentration falls (Figure 6.2). The initial rates of reaction for both azide concentrations are presented in the table on the title page of Figure 6.2

In order to determine an approximate rate at which the reaction between Tc^{V} and azide could occur during the Tc-catalysed oxidation of hydrazine, a reaction was carried out at 298 K and 7 mol dm^{-3} HCl. The calculated rate constant for this reaction was 38.4 dm^{3} mol^{-1} s^{-1}. An aliquot of the yellow reaction mixture containing $[TcNCl_5]^{2-}$ was withdrawn and its esr spectrum was recorded. At 298 K no spectrum was obtained but at 77 K a 10-line Tc centred spectrum was evident. The same esr spectrum was recorded from a sample of a Tc-N_2H_4 reaction mixture and is illustrated in Figure 4.14; this

Figure 6.1 : Changes in the U.V.-visible Spectrum with Time caused by the Oxidation of $[TcOCl_4]^-$ by Azide Ion

$[TcOCl_4]^-$	:	1.6×10^{-3} mol dm^{-3}
$[NaN_3]$	:	2×10^{-3} mol dm^{-3}
[HCl]	:	11.2 mol dm^{-3}
Temp	:	24°C
Path length	:	1 mm

Spectra recorded at 0 s, 33 s, 273 s, 513 s, 993 s and 1953 s.

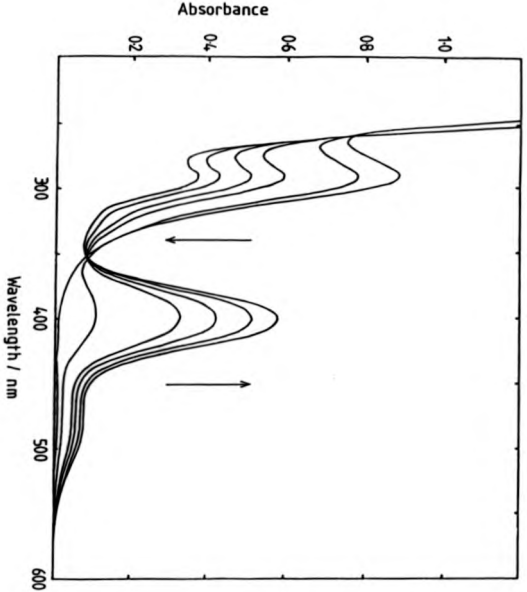
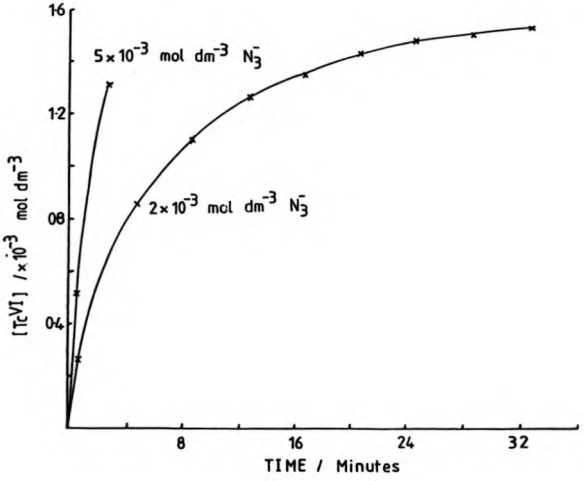

Absorbance
0.2
0.4
0.6
0.8
1.0
300
400
500
600
Wavelength / nm

Figure 6.2 : The Time-evolution of $[TcNCl_5]^{2-}$ at varying Initial Azide Concentration

$[TcOCl_4]^-$	:	1.6×10^{-3} mol dm^{-3}
$[NaN_3]$	:	Varied
[HCl]	:	11.6 mol dm^{-3}
Temp	:	24°C

Table 6.1 : Initial Rates of $[TcNCl_5]^{2-}$ Production with varying Azide Concentration

$[NaN_3]$ / mol dm^{-3}	Rate of Production of $[TcNCl_5]^{2-}$ / mol dm^{-3} s^{-1}
2×10^{-3}	1.3×10^{-6}
5×10^{-3}	3.4×10^{-6}


1·6
1·2
0·8
0·4
5 × 10⁻³ mol dm⁻³ N₃⁻
2 × 10⁻³ mol dm⁻³ N₃⁻
[Tc^VI] /×10⁻³ mol dm⁻³
8
16
24
32
TIME / Minutes

shows that in perchloric acid media this reaction takes place albeit over the course of several days.

6.1.1 Discussion

A similar Tc(VI) nitrido complex has not been detected in nitric acid systems. Several reasons may explain this; in nitric acid the Tc^{V} produced may well take the form of the oxo-complexes such as TcO^{3+} which may react differently with azide. Alternatively, the nitride ligand may be capable of stabilising Tc^{VI} in $[TcNCl_5]^{2-}$ but not a complex such as $[Tc(O)_2N]^{-}$.

If such a complex was produced in nitric acid system, even as a highly unstable transient, then we would observe the Tc^{V} or Tc^{IV}-catalysed oxidation of the azide ion. It is therefore proposed that such a reaction may take place, thus explaining the slow destruction of azide in Tc-hydrazine reaction mixtures.

The oxidation of hydrazoic acid by metal ions such as Co^{III} (131), Mn^{III} (132) and Ce^{IV} (133) is well-established, but in none of these cases is a metal nitride complex formed as the end product of the reaction. For these examples, it was proposed that an inner-sphere oxidation of HN_3 by the metal ion takes place, the azide radicals yielding nitrogen in a bimolecular process. The proposed reaction scheme is given below. (131)

$$Co^{III} + HN_3 \rightleftharpoons Co^{III}HN_3$$

$$Co^{III}HN_3 + HN_3 \xrightarrow{k_1} Co^{II} + \cdot H_2N_6^{+} \qquad \text{slow}$$

$$Co^{III} + \cdot H_2N_6^{+} \xrightarrow{k_2} Co^{II} + 3N_2 + 2H^{+} \qquad \text{fast}$$

The action of Tc^{V}, which is oxidised to Tc^{VI} by hydrazoic acid, is therefore unusual. It is proposed that the hydrazido-technetium(V)

complex produced does not undergo a reaction with a further azide ion to yield the $H_2N_6^+$ radical but instead the complexed azide ion undergoes cleavage to N_2^- and N. The nitride radical so produced then complexes the Tc^V to produce a Tc^{VII} nitride which undergoes a rapid reduction to Tc^{VI}, the proposed pathway being given in the equations below.

$$Tc^V + HN_3 \rightleftharpoons Tc^V HN_3 \qquad \text{slow}$$

$$Tc^V HN_3 \rightleftharpoons Tc^V + N_2H + N^\cdot \qquad \text{slow}$$

$$Tc^V + N^\cdot \rightleftharpoons Tc^{VII} N \qquad \text{very fast}$$

$$Tc^{VII} N \rightleftharpoons Tc^{VI} N \qquad \text{very fast}$$

6.2 The Destruction of Hydrazoic Acid by Photolysis in Azide-HNO_3-TcO_4^-

The photolysis of solutions of sodium azide in nitric acid has been shown to cause a significant decrease in azide concentration. The presence of technetium as pertechnetate enhances this destruction from 17% to 47% after 10 minutes irradiation. The nature of the technetium species produced, which is precipitated from solution as a white solid at high technetium and azide concentrations, is unknown.

A series of solutions were prepared having nitric acid concentrations ranging from 0.1 to 1.2 mol dm^{-3}, but with azide and pertechnetate concentrations being constant. An aliquot of each solution was placed in a 1 cm path-length quartz cell and irradiated using unfiltered light from a 200 W tungsten lamp. After this time an aliquot of the reaction mixture was withdrawn and the amount of azide determined using a spectrophotometric assay based on the

absorbance of a Cu^{II}-azide complex at 375 nm. The results are plotted in Figure 6.3.

From the graph it can be seen that the minimum rate of oxidation of the azide ion occurred at 0.6 mol dm^{-3} acid. At higher nitric acid concentrations, the amount of azide destroyed increased, leading to approximately a 47% destruction at an acidity of 1.2 mol dm^{-3}. Whether this effect is due to increasing the concentration of nitrate ions, protons or both is unknown and further experiments would be necessary in order to elucidate this question.

An experiment in which the light was passed through a glass filter to absorb the ultra violet radiation prior to entry into the quartz cell was carried out. This resulted in only a minimal destruction of the azide, showing that ultra violet light is necessary to excite the pertechnetate ion (λ_{max} at 248 and 288 nm) if the reaction is to occur to any extent. No esr signal was observed during this experiment which was carried out in the presence of the spin trap PBN, similarly no esr signal was obtained when a solution containing no pertechnetate was irradiated with ultraviolet light, thus confirming the role of an excited state pertechnetate ion in the reaction. The esr spectrum obtained (Figure 6.4) shows a multiplet of four peaks centred around g = 2.0 with an identical quadruplet occurring on either side, caused by hyperfine splitting.

The nature of the paramagnetic species produced on photolysis in the presence of TcO_4^- remains uncertain. The major ^{14}N-coupling of 26.9 G indicates an unusually large coupling to ^{14}N for a nitroxide; the quartet must include a doublet coupling from the single proton derived from PBN, split by a second ^{14}N nucleus. The best fit is obtained by invoking the splitting of the energy levels in one ^{14}N nucleus (spin 3/2) by the applied field. These energy levels are

Figure 6.3 : % Destruction of Sodium Azide with varying Nitric Acid Concentration when Photolysed in the presence of Pertechnetate

$[TcO_4^-]$	:	1.0×10^{-3} mol dm^{-3}
$[NaN_3]$	:	0.05 mol dm^{-3}
$[HNO_3]$	:	0.1 - 1.2 mol dm^{-3}
Temp	:	20 - 25°C

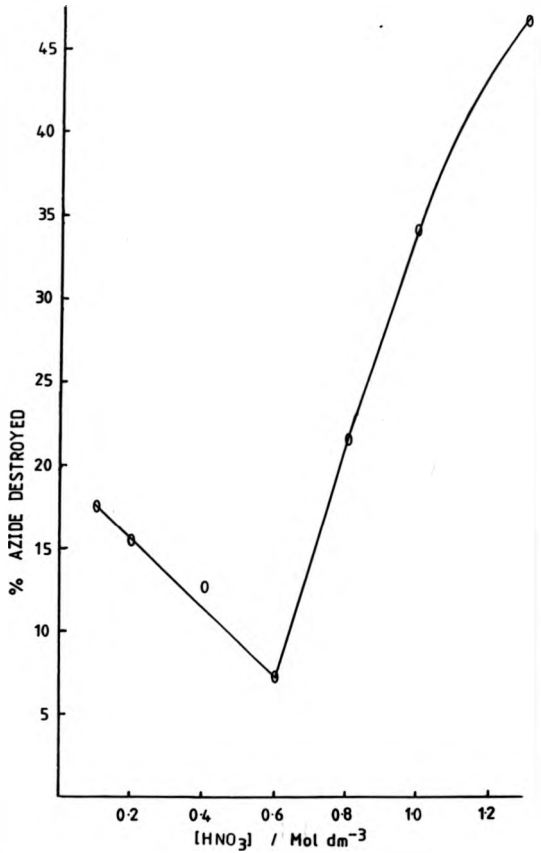
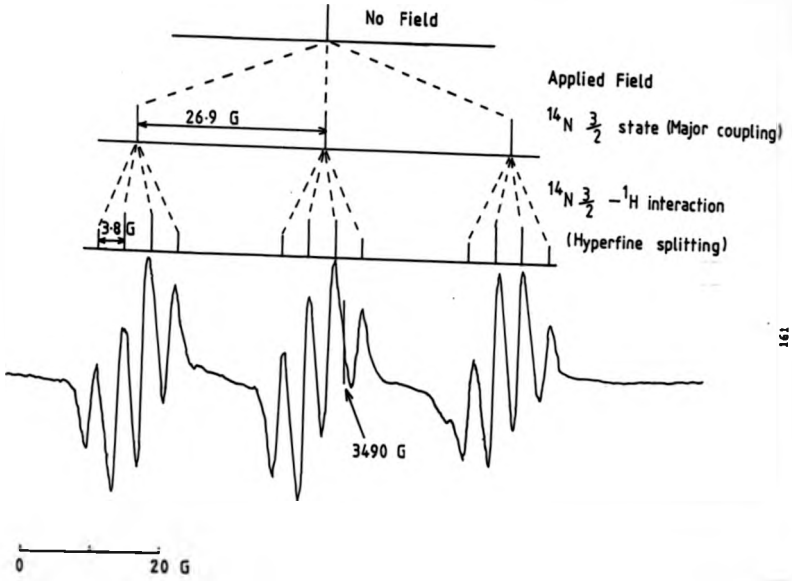
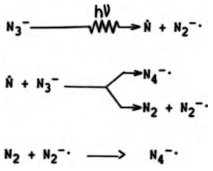

% AZIDE DESTROYED
45
40
35
30
25
20
15
10
5
0·2
0·4
0·6
0·8
1·0
1·2
[HNO3] / Mol dm-3

Figure 6.4 : The Isotropic E.S.R. Spectrum of the Photolysis Product Produced on Irradiation of TcO_4^- and Sodium Azide in the presence of the Spin Trap PBN


No Field
Applied Field
26·9 G
$^{14}N\ \frac{3}{2}$ state (Major coupling)
$^{14}N\ \frac{3}{2} - {}^{1}H$ interaction
(Hyperfine splitting)
3·8 G
3490 G
0
20 G

then further split due to couplings of 3.8 G from one ^{14}N nucleus and one proton, to give a 1:2:2:1 quartet; this also matches the intensity distribution. This is not typical of the couplings found from the spin adduct of the azide radical to PBN, for which Rehorek et al. (135) give $a(^{14}N) = 13.95$ G, $a(^{1}H) = 1.89$ G. The N-centred radical adding to the PBN, could be a new radical such as $N_2^{-\cdot}$ or even $N_4^{-\cdot}$, giving the adduct PBN-$N_2^{-\cdot}$. A reaction scheme invoking such species has been proposed to explain the changes in the esr spectra of X-irradiated single crystals of sodium or potassium azide (134), and is given below



It is considered possible that an excited state pertechnetate ion may attack an azide ion, causing its cleavage into N and $N_2^{-\cdot}$ in a reaction similar to that caused by X-irradiation.

EXPERIMENTAL

7.1 Apparatus

The technetium-hydrazine reactions were carried out in Quickfit conical flasks (50 cm^3) and the gases evolved were passed through a solution of sodium hydroxide (0.1 M) and then collected in an inverted water-filled burette. For the reactions carried out in tetrafluoroborate ion media, plastic conical flasks (Nalgene labware, based on polymethylpentene) were employed as the acid contained HF impurities which etch glass.

7.1.1 Spectrophotometric Measurements

Absorbances at fixed wavelengths were recorded using a Unicam SP 500 series 2 U.V-visible spectrophotometer or a Philips PU 8720 U.V-visible spectrophotometer.

Quartz cuvettes were employed throughout the study with pathlengths varying from 1 mm to 10 cm, except for the tetrafluoroborate samples when disposable plastic cuvettes (10 mm pathlength) were used.

7.1.2 Liquid Scintillation Measurements

Two scintillation counters were used for Tc assays, namely an LKB Rack-beta counter and a Packard Tricarb counter. A commercial scintillation 'cocktail' for aqueous samples was used (LKB Optiphase "Safe")

7.1.3 Materials

7.1.3.1 Technetium(VII) (TcO_4^-)

^{99}Technetium as ammonium pertechnetate was obtained from Amersham International either as a solid or in solution in ammonium hydroxide. The samples supplied in solution form were subjected to a pretreatment to ensure all Tc was present as TcO_4^- and to remove excess ammonium hydroxide. This was achieved by evaporating the

solution to dryness and then refluxing for 4-5 hours in nitric acid (8 M), to prevent any possible laboratory contamination by volatile Tc_2O_7, any gases evolved were passed through a solution of sodium hydroxide. The refluxed technetium solution was diluted after cooling to a standard volume and the technetium content determined radiometrically.

7.1.3.2. Technetium(V)

A Tc^V standard was prepared by adding an aliquot of the standardised pertechnetate to concentrated HCl (11.6 M). This treatment rapidly and completely reduces pertechnetate to $[TcOCl_4]^-$ ion according to the following equation:-

$$TcO_4^- \xrightarrow{HCl} [TcO_3Cl_3]^- \rightarrow [TcOCl_4]^-$$

Any dilutions of this solution were carried out using concentrated HCl to maintain the acidity, as the Tc^V complex is unstable at acidities below 3M HCl.

7.1.3.3 Technetium(IV)

An aliquot of the standardised TcO_4^- solution (0.5 cm^3, 0.08 M) was added to HCl (11.6 M), powdered potassium iodide was added (in a ratio of 1 mg NH_4TcO_4 to 1 mg KI). The brown-purple solution was heated to near boiling for 30 minutes. During boiling, concentrated hydrochloric acid was added to replace any acid lost. The mixture was cooled and left to stand overnight. The reaction mixture was boiled again to reduce the volume and to remove liberated iodine. The remaining liquid was removed by decantation (with a teat pipette), and HCl (50 cm^3, 11.6 M) was added and the mixture heated to simmering point for 5-6 hours. The resulting golden-orange solution was boiled to reduce its volume to about 5 cm^3.

7.1.3.4 Hydrazine

Hydrazine nitrate was prepared by neutralising hydrazine hydrate (A.R. grade, BDH Chemicals) with concentrated nitric acid, (16 M) and diluting to 5.8 M (the reaction is very exothermic). Hydrazine hydrate stock solutions were prepared by diluting the hydrazine hydrate to 5.8 M with distilled water.

7.1.3.5 Other Chemicals

All other reactants used were of A.R. quality unless indicated otherwise and were used without further purification. The water used was doubly distilled.

7..2 Analytical Procedures

7.2.1 Technetium Assay using Liquid Scintillation

The isotope ^{99}Tc decays by β-emission ($t_{\frac{1}{2}}$ 2.12 x 10^5 years, 0.292 MeV) and can be determined using the ^{14}C and ^{32}P counting channels in a commercial spectrometer. A radiometrically certified standard sample of ammonium pertechnetate in ammonium hydroxide (0.01 M) was obtained from Amersham International; from this standard a calibration curve was constructed for technetium assays, the degree of quenching being determined using the external standard channels ratio.

7.2.2 Technetium(V) Assay

The concentrations of both technetium(IV) and (V) were determined using the thiocyanate colorimetric analysis developed by Howard and Weber (109). An aliquot of Tc^{IV} or Tc^{V} solution was added to a solution of ammonium thiocyanate. Technetium(IV) forms a yellow complex and Tc^{V} a red complex; Tc^{VI} and Tc^{VII} do not react. The two complexes mutually interfere, but can be readily separated by the complete solvent extraction of the Tc^{V} complex into n-butyl acetate.

An aliquot (0.5 cm^3) of the technetium(V) solution was added to an aliquot of the ammonium thiocyanate solution (4.5 cm^3, 0.33 M), and the resulting mixture was left for 40 minutes, after which the concentration of the red species $[Tc(NCS)_6]^{2-}$ had reached a maximum. The complex was extracted into butyl acetate and the two phases were separated using a pasteur pipette containing a plug of cotton wool to act as a moisture filter. For the calibration curve, the absorbance was measured at 513 nm and a molar extinction coefficient of 50 000 $dm^3\ mol^{-1}\ cm^{-1}$ was obtained. This is exactly the same value obtained by Howard and Weber (109). Garraway and Wilson (15) diluted the butyl acetate phase with acetone and obtained an extinction coefficient of 47 700 $dm^3\ mol^{-1}\ cm^{-1}$. When the latter method was used by us, some of the solutions developed traces of a white precipitate and so the original assay derived by Howard and Weber was adopted. The calibration curve obtained for the complex is given in Figure 7.1.

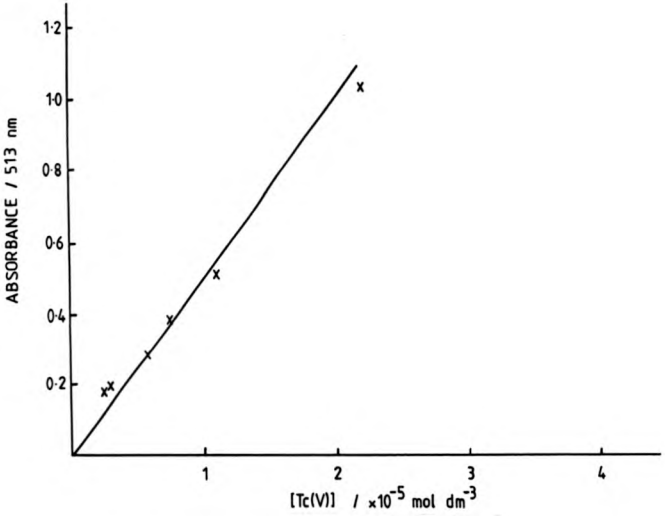
7.2.3 Technetium(IV) Assay

The assay for Tc^{IV} was carried out as for Tc^{V}. An aliquot of the Tc^{IV} solution was added to an ammonium thiocyanate solution, and after shaking with butyl acetate the absorbance of the yellow aqueous phase was measured at 430 nm. An extinction coefficient of 9500 $dm^3\ mol^{-1}\ cm^{-1}$ was calculated, agreeing reasonably closely with the value of 10 000 $dm^3\ mol^{-1}\ cm^{-1}$ obtained by Garraway and Wilson (15).

7.2.4 Hydrazine Assay

Hydrazine was assayed using a colorimetric analysis developed by Watt and Chrisp (110). This method employs the colour reagent p-dimethylaminobenzaldehyde (PDMAB) (Ehrlich's reagent), which forms a yellow-orange, quinoidal azine condensation product

Figure 7.1 : Calibration Curve obtained for the Thiocyanate Colorimetric Analysis of Tc^{V}


ABSORBANCE / 513 nm
1·2
1·0
0·8
0·6
0·4
0·2
1
2
3
4
[Tc(V)] / ×10⁻⁵ mol dm⁻³

with λ_{max} at 468 nm. Beer's law being obeyed over a concentration range of 1 x 10^{-6} - 1 x 10^{-4} mol dm^{-3}. Several developments of the original method have been reported, thus Martin reduced the acidity to 0.4 M hydrochloric acid (as opposed to the 1.0 M concentration used by Watt and Chrisp), allowed 10 minutes for colour development and extracted the azine into chloroform(111). He reported an extinction coefficient of nearly 60 000 dm^3 mol^{-1} cm^{-1} at 490 nm. This method was further modified by Embleton and Wilson by measuring the absorbance of the azine without extraction into chloroform, thus increasing the speed of analysis as the low levels of radioactivity present were not considered to constitute a health hazard (112).

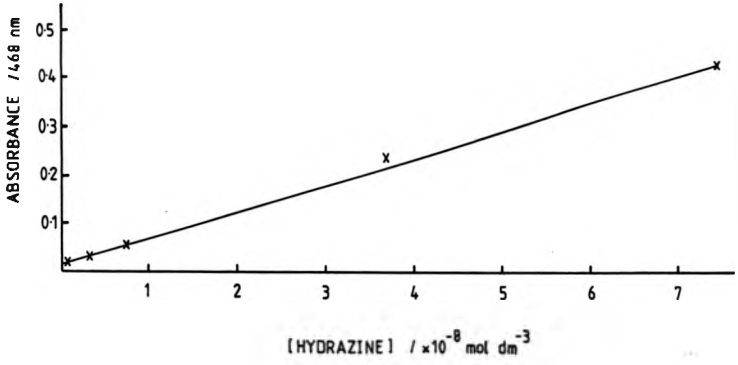
We adopted the Embleton and Wilson modification of the Martin procedure. The colour was developed by adding an aliquot (0.5 cm^3) of the hydrazine solution to a volumetric flask (50 cm^3) and making up to the mark with the following mixture: 2% PDMAB in industrial methylated spirit (IMS) (10 cm^3), 0.3 M hydrochloric acid (10 cm^3) and IMS (30 cm^3). After approximately 45 minutes the absorbance was measured at 468 nm. An extinction coefficient of 60 400 dm^3 mol^{-1} cm^{-1} was obtained from the calibration curve (Figure 7.2) in excellent agreement with Martin (111).

7.2.5. Ammonium Ion Assay

Ammonia was determined using the phenol-hypochlorite method (113), which is sensitive over an ammonia concentration range of 6 x 10^{-6} to 2 x 10^{-3} mol dm^{-3}.

An aliquot of the sample (normally 0.5 cm^3) was added to 5 cm^3 of a solution of phenol and sodium nitroprusside (5 g and 20 mg in 500 cm^3 respectively) and 5 cm^3 of a solution containing sodium hydroxide and sodium hypochlorite (5 g and 2.5 cm^3 10% available chlorine in 500 cm^3 respectively). The resulting solution was

Figure 7.2 : Calibration Curve obtaianed for the Hydrazine Assay using PDMAB


ABSORBANCE /468 nm
0·5
0·4
0·3
0·2
0·1
1
2
3
4
5
6
7
[HYDRAZINE] / ×10⁻⁸ mol dm⁻³

incubated at 35°C for 45 minutes to allow full colour development and the absorbance measured at 625 nm. The concentrations of ammonia in samples were calculated from the calibration curve (Figure 7.3), from which an extinction coefficient of 21570 dm^3 mol^{-1} cm^{-1} was obtained. An investigation into the possible use of Nessler's reagent as an alternative assay was carried out but this was not employed due to interference by hydrazine.

7.2.6 Azide Ion Assay

Azide can be determined colorimetrically using copper(II) ions; the CuN_3^+ product is formed quantitatively and we determined an extinction coefficient of 1570 dm^3 mol^{-1} cm^{-1} (λ_{max} 375 nm). This agrees closely with the value of 1600 dm^3 mol^{-1} cm^{-1} given by Neves et al. (114) at this wavelength. The procedure used was as follows; acetate buffer (1 cm^3; 1 M sodium acetate, 0.1 M acetic acid) was added to a volumetric flask (10 cm^3); an aliquot of the azide solution (0.5 cm^3) was added followed by copper nitrate solution in HNO_3 (3 cm^3; 0.92 M in 1 mM HNO_3). After 20 minutes the absorbance was recorded at 375 nm.

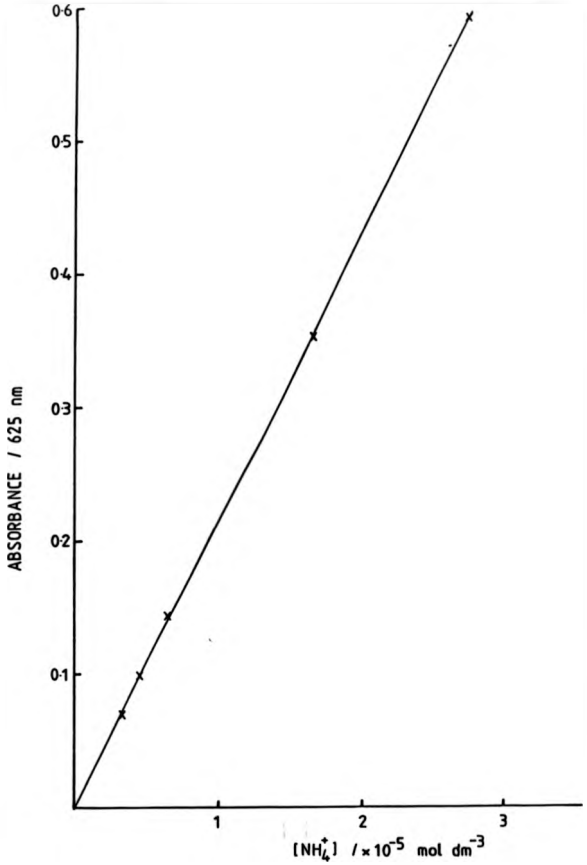
7.2.7 E.S.R. Spectra

Esr spectra were recorded using two instruments, namely a Bruker Model ER 200 tt and a Bruker Model ER 200.

Room temperature spectra of solutions and spectra of photolysis products were recorded using a flat quartz cell with a path length of 0.1 mm. To obtain spectra of aqueous solutions at low temperatures it was necessary to add ethanol (1:1 ratio ethanol : sample) to ensure a frozen glass was obtained rather than a crystalline matrix. The resulting solution was placed in a quartz tube approximately 2 mm internal diameter; this was then placed in a quartz dewar containing liquid nitrogen which was seated in the

microwave cavity.

Figure 7.3 : Calibration Curve for the Determination of Ammonium Ions using the Phenol-Hypochlorite Analysis.


0·6
0·5
0·4
0·3
0·2
0·1
ABSORBANCE / 625 nm
1
2
3
[NH4+] / × 10-5 mol dm-3

SUGGESTIONS FOR FURTHER WORK

A large number of intermediates of varying stability have been noted from the U.V.-visible and esr spectra of reaction mixtures, and it is felt desirable to place some of these assignments on a firmer footing. Isolation of crystalline materials may be possible in some instances, using suitable precipitating ions, enabling perhaps X-ray crystal structure determination to be achieved.

The investigation of systems containing pertechnetate and hydrazine in non-oxidising acid media should be studied in greater depth to enable the effects of acidity on the reaction to be elucidated more fully. The addition of nitrate or perchlorate to such sytems will then enable the effects of these oxidants to be segregated and the development of a cyclic reaction scheme to be formulated.

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APPENDIX

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App I + II